

# **THE EFFECT OF CONDITIONING ON FROTH FLOTATION**

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# SYNOPSIS

The method and extent to which mineral slurries are conditioned have been shown to greatly affect flotation grades and recovery. Most of this work is very mineral specific and centres around one or two operating variables. One of the major obstacles to understanding the effects of such pretreatment more fully, and to developing a global understanding of conditioning, is the system specific nature of the procedures applied to each mineral, and the apparently conflicting results across a range of mineral types.

This thesis sets out to define conditioning both broadly enough to encompass almost all aspects of conditioning, as well as specifically enough to be useful in the study of single mineral-collector systems. Having done this, a measure of the efficiency or effectiveness of conditioning is devised and used to evaluate the relative effects of variables of conditioning, as well as to gain some insight into the mechanisms affecting the results. The work is completed by relating these observations to expected results in industrial applications and their implications on plant procedures.

Most forms of conditioning for flotation were found to fit into two basic categories, which if they both take place in the same process, follow one another sequentially. In this thesis, these were termed "primary" and "secondary" conditioning, and were defined as follows:

*Primary Conditioning relates to the physical preparation of the surface of the particles, including comminution, oxidation, acid leaching and bacterial pretreatment.*

*Secondary Conditioning is the process whereby prepared particles are rendered hydrophobic or hydrophilic through mixing, control of the environment and contacting with reagents.*

It was also found in the literature that primary conditioning is very ore specific, while secondary conditioning is almost universally applied. For this reason, the present work concentrates on the most common aspect of secondary conditioning, namely the **adsorption of collector onto the mineral surface in order to render it hydrophobic for flotation**. In most instances, this is carried out as a heterogeneous stirred tank reaction, with a surface reaction (adsorption of collector onto a mineral surface) as the primary event. The variables most likely to affect such a process were considered to be (the variables tested in this work are indicated by italics):

ORE :	Mineral type and degree of liberation Grind size, affecting such features as surface to volume ratio <i>Pulp density</i>
COLLECTOR :	<i>Type, including solubility, polarity and molecule size</i> <i>Dosage</i> <i>Attachment mechanism</i>
SYSTEM :	pH <i>Time</i> <i>Mixing (power and turbulence)</i> <i>Method of agitation (turbulence distribution)</i> Temperature <i>Ionic Strength</i>

Having thus defined conditioning, and identified the factors most likely to affect it, it was necessary to devise a measure of conditioning efficiency or effectiveness (since none exists) to be able to evaluate the relative effects of the variables of conditioning.

Previous work was critically analyzed to gain a better understanding of how conditioning might be measured. In particular, the thesis of F.J.N. Stassen [1990] was scrutinised. The analysis showed that it would be necessary to divorce flotation from the test procedure, if conditioning effects were to be isolated from the complicating factors of the flotation pulp and froth phases. Hence the measurement of conditioning was divided into two aspects:

- 1) The measurement of collector adsorption
- 2) The measurement of flotation response of given levels of adsorption

Adsorption of collector was measured indirectly using UV spectrophotometry. This was used to measure the removal of collector from solution, from which adsorption onto the mineral surface was inferred (by difference).

Microflotation was chosen as the technique used to relate flotation response to adsorption. The advantage of microflotation over other flotation systems, is its use of very small quantities of mineral and the ability to operate the system without the complicating froth phase.

The mineral-collector system finally chosen for the test work was pyrite-thiols. There were a number of advantages to using this system over many others, including the applicability of

this system to industry and the large body of literature available on topic. The adsorption reactions are however complex and not completely understood.

The test work was carried out using gravity concentrated pyrite milled to  $+75-106\ \mu\text{m}$  and two thiol collectors, potassium n-butyl xanthate and sodium n-propyl dithiocarbamate. Samples were conditioned in a specially designed baffled cylindrical vessel, agitated by a pitched blade impeller. The power input into conditioning could be varied by altering the impeller rpm, or the conditioning time. The test program investigated the effects on the efficiency of conditioning of all the variables indicated above.

The variables found to have the greatest effect on conditioning results are as follows:

Effect of Collector Type - It was shown that different collectors adsorb onto the mineral surface at different rates and may have different equilibrium levels of adsorption. How this affects collector choice depends on the kinetics of the system and the extent of conditioning provided by the plant operated.

Effect of Duration and Power of Conditioning - The duration and power input into conditioning were found to be the most important variables affecting adsorption. Previous work suggested that energy input was of primary importance. This work, however, shows both theoretically and practically that this is not the case. Rather, the manner in which the energy is added, either through duration or power, is more crucial and depends largely on whether the system is diffusion rate controlled or surface reaction rate controlled. The optimal energy input for a plant could be calculated using a costing function.

Effect of Collector Concentration and Pulp Density - Varying concentration and pulp density led to some unexpected findings. The collector used in most of the tests was found to ionise only weakly and hence the reaction rate constant was adversely affected by increasing collector doses. The partial ionisation also resulted in the total lack of any advantage to be found by increasing pulp density, concentrating the collector without increasing dosage. Nevertheless, overdosing with collector was shown to provide the required adsorption within a much shorter conditioning period, than would otherwise be required for the minimum necessary dosage.

The work showed that conditioning is controlled by the factors pertaining to heterogeneous stirred tank reactions. While the actual importance of each variable is specific to the

application and conditions used, they are all explained in terms of the adsorption of collector onto the mineral surface. Hence, the relative importance of diffusion and of the reaction, in controlling adsorption rate, determines the variables to be considered when optimising conditioning. With all variables, there is a trade-off between improved conditioning and increased costs. Use of a costing function appears to be the best method of optimising conditioning in industrial applications.

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# TABLE OF CONTENTS

<b>SYNOPSIS</b> .....	i
<b>ACKNOWLEDGEMENTS</b> .....	v
<b>TABLE OF CONTENTS</b> .....	vi
<b>LIST OF FIGURES</b> .....	x
<b>CHAPTER 1 - INTRODUCTION</b> .....	1
1.1. Background .....	1
1.2. Research Outline .....	2
<b>CHAPTER 2 - LITERATURE REVIEW</b> .....	4
2.1. Introduction .....	4
2.2. Principles of Flotation .....	4
2.2.1. Flotation Sub-processes .....	6
2.2.1.1. Conditioning of the Ore .....	6
2.2.1.2. Attachment of Mineral Particles to Bubbles .....	7
2.2.1.3. Froth Formation and Removal .....	7
2.3. Definition of Conditioning .....	7
2.4. The Structure of Collectors .....	11
2.4.1. Anionic Collectors .....	12
2.4.2. Cationic Collectors .....	13
2.5. Stages in Conditioning .....	14
2.5.1. Diffusion to the mineral surface .....	15
2.5.2. Displacement of water .....	16
2.6. Thermodynamics and Kinetics of Conditioning and Flotation .....	18
2.6.1. Thermodynamic Criterion for Conditioning .....	18
2.6.2. Kinetic Criterion for Conditioning .....	21
2.7. Mathematical Modelling of Flotation - The Klimpel Flotation Model .....	24
2.8. Shear-flocculation .....	26
2.9. Research in Conditioning .....	28
2.9.1. Stassen .....	33
2.9.2. Ralston .....	37



2.9.2.1.	Flotation as a function of particle size and surface coverage .....	37
2.9.2.2.	Influence of Ionic Strength on Flotation Response .....	40
2.9.2.3.	Flotation recovery as a function of time .....	41
2.10.	Summary .....	42
<b>CHAPTER 3 - CRITIQUE OF STASSEN'S WORK .....</b>		<b>45</b>
3.1.	Introduction .....	45
3.2.	Experimental Technique .....	45
3.3.	Derivation of Stassen's Model .....	47
3.4.	Stassen's Results and Regressed Model .....	52
3.5.	The Model's Assumptions .....	53
3.6.	Continued Conditioning During Flotation .....	60
3.7.	Reproducibility .....	66
3.8.	Graphical Re-Interpretation of Data - the Importance of Power and Time vs Energy .....	66
3.9.	Attrition Mechanism .....	70
3.10.	Conclusion .....	71
<b>CHAPTER 4 - DEVELOPMENT OF APPROPRIATE TECHNIQUES FOR MEASURING THE EFFECTIVENESS OF CONDITIONING .....</b>		<b>73</b>
4.1.	Introduction .....	73
4.2.	Adsorption as a Measure of Conditioning .....	74
4.2.1.	Surface and Monolayer Coverage .....	75
4.2.2.	Measuring Residual Collector in Solution .....	77
4.2.3.	Choice of an Appropriate Mineral-Collector System .....	78
4.2.3.1.	Quartz-Amine System .....	78
4.2.3.2.	Pyrite-Thiol System .....	78
4.3.	Relating Adsorption to Flotation: Microflotation .....	83
4.4.	Experimental Equipment and Procedures .....	84
4.4.1.	Conditioning Tests .....	84
4.4.1.1.	The Conditioning Vessel .....	84
4.4.1.2.	Power Input .....	87
4.4.1.3.	Collector Addition Point .....	88
4.4.1.4.	Experimental Procedure .....	88
4.4.2.	Adsorption Response .....	90
4.4.3.	Flotation Response .....	92

4.4.3.1.	Microflotation cell . . . . .	92
4.4.3.2.	Experimental Procedure . . . . .	93
4.5.	Preliminary Work . . . . .	94
4.5.1.	Quartz-Amine Adsorption . . . . .	94
4.5.1.1.	Measurement of concentrated solutions of HPYC . . . . .	95
4.5.1.2.	Measurement of dilute solutions of HPYC . . . . .	97
4.5.1.3.	Absorbency of conditioned slurry with no collector added . . . . .	97
4.5.1.4.	Conclusions on amine absorbency spectra . . . . .	98
4.5.2.	Quartz-Amine Microflotation . . . . .	99
4.5.2.1.	Reproducibility . . . . .	99
4.5.2.2.	Effect of collector dosage . . . . .	100
4.5.2.3.	Effect of conditioning time . . . . .	101
4.5.2.4.	Shear-flocculation . . . . .	103
4.5.3.	Pyrite-Thiol Microflotation . . . . .	103
4.5.4.	Pyrite-Thiol Adsorption . . . . .	109
4.6.	Conclusion . . . . .	113
<b>CHAPTER 5 - DEFINING THE EXPERIMENTAL PROGRAM . . . . .</b>		<b>116</b>
5.1.	Introduction . . . . .	116
5.2.	Variables to be Studied . . . . .	116
5.3.	Experiments Chosen . . . . .	119
5.3.1.	Effect of Collector Type . . . . .	119
5.3.2.	Time and Power Effects of Conditioning . . . . .	119
5.3.3.	Effect of Type of Power Input (Volume) . . . . .	123
5.3.4.	Collector Concentration . . . . .	123
5.3.5.	Water content . . . . .	123
5.4.	Summary of Tests to be Performed . . . . .	124
<b>CHAPTER 6 - RESULTS AND DISCUSSION . . . . .</b>		<b>125</b>
6.1.	Introduction . . . . .	125
6.2.	Effect of Collector Type . . . . .	125
6.3.	Reaction Mechanisms of Adsorption . . . . .	127
6.4.	Time Effects of Conditioning . . . . .	129
6.5.	Power Effects of Conditioning . . . . .	130
6.6.	Effect of Type of Power Input . . . . .	132
6.7.	Relationship between Time, Power and Energy . . . . .	133

6.8. Effect of Collector Concentration .....	136
6.9. Influence of Pulp Density .....	139
6.9.1. Slow Ionisation of the Collector .....	141
6.9.2. Ionisation Constant of the Collector .....	142
6.10. Correlation between conditioning and flotation results .....	145
6.11. Limitations of this Work .....	146
 <b>CHAPTER 7 - CONCLUSIONS</b> .....	 149
 <b>REFERENCES</b> .....	 154
 <b>APPENDIX A. - Derivation of Expression for R in Stassen's Equations</b> .....	 A1
 <b>APPENDIX B. - Stassen's Experimental Data</b> .....	 A3
 <b>APPENDIX C. - Surface Area Calculations</b> .....	 A6
 <b>APPENDIX D. - Quartz-Amine Microflotation Test Data</b> .....	 A8
 <b>APPENDIX E. - Pyrite-Thiol Microflotation Test Data</b> .....	 A12
 <b>APPENDIX F. - Pyrite-Thiol Adsorption Test Data</b> .....	 A14

# LIST OF FIGURES

Figure 2.1 - Basic Schematic of the Flotation Process . . . . .	5
Figure 2.2 - Schematic of Flotation Showing Conditioning . . . . .	9
Figure 2.3 - Macro-Scale Representation of Conditioning . . . . .	10
Figure 2.4 - Relationship Between Collector in Solution and on the Surface . . . . .	12
Figure 2.5 - Structure of Potassium Ethyl Xanthate . . . . .	13
Figure 2.6 - The Electronic States of a Xanthate . . . . .	14
Figure 2.7 - Hydrophilic Mineral . . . . .	15
Figure 2.8 - Mineral Is Made Hydrophobic . . . . .	15
Figure 2.9 - Liquid Phases Surrounding Particle . . . . .	16
Figure 2.10 - Adsorption Rate vs Agitation . . . . .	17
Figure 2.11 - Free Energy vs Distance From Particle Surface . . . . .	19
Figure 2.12 - Effect of Hydrophobicity on Free Energy Changes . . . . .	20
Figure 2.13 - Collector-Surfactant Interaction (from Leja and Schulman, 1954) . . . . .	24
Figure 2.14 - Relative Importance of Klimpel k and R Parameters . . . . .	26
Figure 2.15 - Effects of Increased k and R Values on Recovery (Yield) . . . . .	26
Figure 2.16 - Hydrophobic Interaction of Shear-Flocculated Particles [Shouci and Song, 1991] . . . . .	27
Figure 2.17 - Effect of Impeller Speed on Rate of Flotation [Duchen, 1980] . . . . .	29
Figure 2.18 - Effect of Impeller Speed on Equilibrium Recovery [Duchen, 1980] . . . . .	29
Figure 2.19 - Effect of Method of Collector Addition on Flotation Response [Von Holt, 1992] . . . . .	31
Figure 2.20 - Effect of Collector Dosage and Impeller Speed on Flotation Response [Von Holt, 1992] . . . . .	32
Figure 2.21 - Effect of Cell Size on Flotation Response [Von Holt, 1992] . . . . .	33
Figure 2.22 - Klimpel Parameters for Sulphur vs Conditioning Energy (from Stassen, 1991a) . . . . .	35
Figure 2.23 - Klimpel Parameters for Gold vs Conditioning Energy (from Stassen, 1991a) . . . . .	36
Figure 2.24 - Klimpel Parameters for Uranium vs Conditioning Energy (from Stassen, 1991a) . . . . .	36
Figure 2.25 - Effect of Surface Coverage on Flotation [Crawford and Ralston, 1988] . . . . .	38
Figure 2.26 - Flotation Recovery as a Function of Surface coverage and Particle Size [Crawford and Ralston, 1988] . . . . .	39

Figure 2.27 - Critical Surface Coverage for Flotation as a Function of Particle Size [Crawford and Ralston, 1988] . . . . .	40
Figure 2.28 - Effect of Ionic Strength on Flotation Recovery [Crawford and Ralston, 1988] . . . . .	41
Figure 2.29 - Time Dependence of Recovery [Crawford and Ralston, 1988] . . . . .	42
Figure 3.1 - Mineral Floated vs Flotation Time . . . . .	60
Figure 3.2 - % Mineral Receiving Continued Conditioning vs Time . . . . .	61
Figure 3.3 - Effect of Conditioning Energy Input on Stassen's Klimpel Parameters Showing $K_{\text{apparent}}$ and $K_{\text{real}}$ . . . . .	64
Figure 3.4 - Klimpel k vs Energy for Sulphur, Colour Separated wrt Time (modified from Stassen) . . . . .	69
Figure 3.5 - Klimpel k vs Energy for Gold, Colour Separated wrt Time (modified from Stassen, 1990) . . . . .	70
Figure 4.1 - Structure of HPYC . . . . .	79
Figure 4.2 - Stable States of Dithiocarbamates . . . . .	82
Figure 4.3 - Design of Axial Flow Impeller . . . . .	87
Figure 4.4 - Partidge and Smith Microflotation Cell . . . . .	93
Figure 4.5 - UV Absorbency Plot for HPYC . . . . .	96
Figure 4.6 - Reproducibility Data Showing % Yield for Each Sample . . . . .	100
Figure 4.7 - Microflotation Yield vs Collector Dosage . . . . .	101
Figure 4.8 - Microflotation Yield vs Conditioning Time . . . . .	102
Figure 4.9 - Pyrite Flotation Yield vs diC3 DTC Collector Dosage (near mono- layer) . . . . .	106
Figure 4.10 - Flotation Response for Collector and Frother (from Austin and Henwood, 1991) . . . . .	107
Figure 4.11 - Collector Dosage vs Flotation Yield (high doses) . . . . .	108
Figure 4.12 - Reproducibility Tests Showing Collector Uptake vs Time for DiC3 DTC . . . . .	112
Figure 4.13 - Reproducibility Tests Showing Collector Uptake vs Time for PNBX . . . . .	113
Figure 5.1 - Experimental Design Matrix . . . . .	121
Figure 6.1 - Adsorption Profiles of Three Thiol Collectors . . . . .	126
Figure 6.2 - Log of Collector Uptake vs Time for DiC3 DTC and PNBX . . . . .	130
Figure 6.3 - Effect of Impeller Speed on diC3 DTC Adsorption . . . . .	131
Figure 6.4 - Effect of Impeller Speed on PNBX Adsorption . . . . .	132
Figure 6.5 - Effect of Power Type on DiC3 DTC Adsorption . . . . .	133
Figure 6.6 - Effect of Eight Times Energy Input using DiC3 DTC . . . . .	134
Figure 6.7 - Effect of Eight Times Energy Input Using PNBX . . . . .	135

Figure 6.8 - Effect of Collector Dosage on DiC3 DTC Adsorption . . . . .	136
Figure 6.9 - Effect of Collector Dosage on PNBX Adsorption . . . . .	137
Figure 6.10 - Effect of Collector Concentration on DiC3 Adsorption Rate Constant .	138
Figure 6.11 - Effect of Pulp Density on diC3 DTC Collector Adsorption . . . . .	140
Figure 6.12 - Effect of Pyrite Content on diC3 DTC Collector Adsorption . . . . .	142

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# **CHAPTER 1 - INTRODUCTION**

## **1.1. Background**

An important but frequently overlooked aspect in the flotation of minerals is the conditioning of the ore. Conditioning provides the environment in which reagent molecules attach to particles, thereby altering their surface properties. The probability of reagent reaching the particle surface is a function of factors such as the intensity and duration of agitation and the concentration of reagent, while the efficiency of subsequent attachment may be a function of the size distribution of the particles and the electrical charges on the particle and reagent molecules, respectively.

It has been shown that the total recovery and flotation rate of gold, uranium oxide and pyrite increase substantially when the conditioning energy is increased [Stassen, 1990]. Moreover, in column flotation test work on South African Witbank coals it has been found that the method of conditioning has a very marked influence on the results obtained [Von Holt, 1992].

The importance of conditioning is highlighted in column flotation since there is no impeller in the cell to provide mixing as is the case in conventional sub-aeration cells. Thus it is crucial that the ore is adequately conditioned prior to introduction into the column. In conventional flotation cells, reagent is frequently added to the first cell in a bank of sub-aeration cells, the cell essentially acting as a conditioning vessel.

While conditioning effects are known to be important in the flotation process, conditioning is still a poorly understood sub-process. The aim of the present work is to isolate the variables of conditioning and to determine the effect of these variables on the efficiency of the conditioning sub-process, and hence on flotation results. The key question to the work can thus be posed as follows:

**"What is the effect of variables of conditioning on conditioning efficiency?"**

This question presupposes that a precise definition of conditioning and of conditioning efficiency exists, and that measures of determining conditioning efficiency are available. As will be shown below, no generally agreed definition of conditioning or conditioning efficiency exist. Moreover, the determination of "conditioning efficiency" is

complicated by the fact that conditioning must be isolated from the flotation process to eliminate masking of effects. Thus answering the key question requires that a number of separate steps be undertaken:

- (1) Clearly define conditioning.
- (2) Determine a useful measure of conditioning efficiency.
- (3) Evaluate the effect of conditioning variables on efficiency.
- (4) Determine the effect of these variables in flotation by correlating conditioning and flotation results.

It is this that the remainder of this thesis aims to do.

## 1.2. Research Outline

The research began by carrying out a literature survey, in which the work of previous researchers in the area of conditioning was studied in depth. This is covered in Chapter 2. A readily available and most detailed investigation is that of F.J.N. Stassen [1990, 1991a, 1991b], who studied the effect of a number of conditioning parameters on gold, uranium oxide and pyrite flotation. Because of the direct relevance of Stassen's investigation to the current study, and the completeness of the data available in his Master's thesis [Stassen, 1990], a critique of the work has been compiled and forms the basis of Chapter 3. In that chapter, the merits and failings of Stassen's experimental technique, results and conclusions are discussed in detail.

Subsequently a number of possible methods of measuring conditioning were explored. The technique most suitable was chosen, and preliminary experimental test work using adsorption and microflotation was performed. This work is detailed in Chapter 4. One of the aims of this work was to choose an appropriate mineral/collector system for more detailed study. In order to avoid complications caused by variations in ore type and sample, the experiments were carried out initially using a quartz-amine test system. This system is widely used when it is desirable to decouple ore type from other effects. Unfortunately, difficulties of measurement made this system impractical for the study of conditioning (reasons for this are outlined in Chapter 4). Work therefore continued using the more complex sulphide system of pyrite and thiol collectors. This system has



also been studied in depth, but the attachment mechanisms are more complex and less well understood. Chapter 4 outlines the preliminary work to determine the appropriate thiol collector dosage for the conditioning tests, and the optimum wave-length at which to measure residual collector concentrations for each collector.

In Chapters 5 and 6, the effects of various physical and chemical parameters on the conditioning of the pyrite ore were investigated. These included: duration and power of mixing, (thiol) collector type and dosage, mechanism of collector attachment and finally mixing method. While all of these variables have been studied individually in detail by others, no attempt has been made previously to study a number of these variables simultaneously in order to evaluate the conditioning process per sé. Chapter 5 discusses the choice of tests to be performed, while Chapter 6 details the results of these tests, and discusses how the results relate to the theoretical background. The implication of these results when designing conditioning stage equipment is also covered.

Finally, Chapter 7 lays out the conclusions reached on the effects of conditioning on froth flotation.

## **CHAPTER 2 - LITERATURE REVIEW**

*The theory of flotation is complex and not completely understood. (Wills, 1988)*

### **2.1. Introduction**

This chapter discusses the findings of literature available on the aspects of flotation relevant to the study of conditioning. It begins with an overview of flotation, covering the basic sub-processes (section 2.2). Following in section 2.3 is a more in-depth discussion on conditioning, from which a useful definition of conditioning is extracted. This definition is used to isolate the aspect of conditioning that will be studied in this thesis.

Because the structure of collectors strongly affects the conditioning process, these are discussed in some detail in section 2.4. The variables of conditioning are then identified in section 2.5 by analysing the steps associated with the conditioning sub-process. This is followed by a discussion on how these variables are expected to affect the thermodynamics and kinetics of conditioning (section 2.6). The effect of these variables can be modelled, to allow easy interpretation of their relative magnitudes, using the Klimpel Flotation Model. How the model does this is described in section 2.7, along with a brief discussion on the theoretical basis for this model and its advantages and failings. One final observed effect, which lies outside of the standard kinetic and thermodynamic models, is shear-flocculation, which is experienced in certain very turbulent systems. How this might affect experimental results is discussed in section 2.8.

Finally, the results of previous studies into how all of these aspects of conditioning and flotation affect conditioning are presented in section 2.9. This section also gives an overview of conditioning research performed to date.

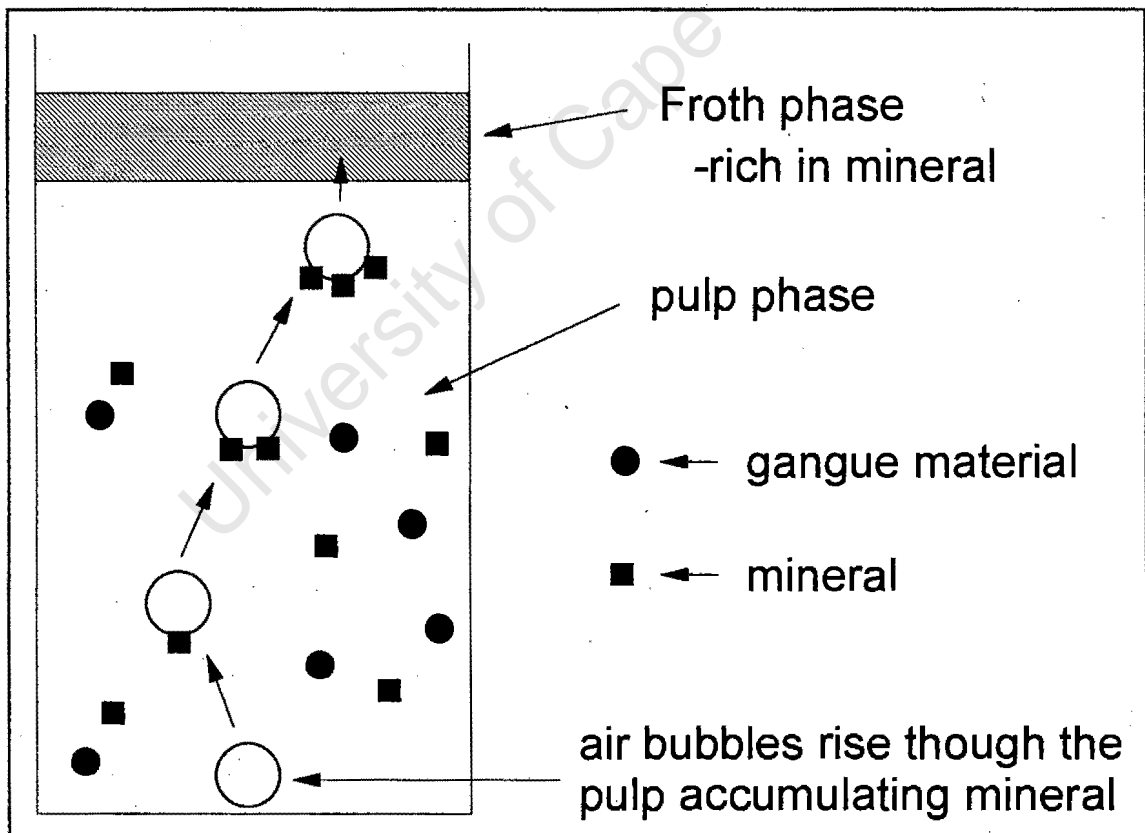
### **2.2. Principles of Flotation**

Flotation is the most important and versatile mineral-processing technique, with millions of tons of mixed solids processed daily to concentrate mineral values. Its applications range from relatively simple mineral separations such as sulphide ore concentration to

complex systems such as copper-lead-zinc separation and fine coal beneficiation. Other uses of flotation include biochemical and polymer separations, the purification of sewage water and the de-inking of recycled paper [Hickey, 1982].

Froth flotation utilises the differences in physico-chemical surface properties of the particles to be separated, especially differences in hydrophobicity. Bubbles rise through a heterogeneous solid-liquid suspension, accumulating certain of the solid particles, which attach by virtue of their hydrophobicity. The hydrophobic solid which attaches to the bubble is thus removed from the solid-liquid suspension. In mineral flotation the removed solid is usually the desired product which is concentrated from a mixture of solids in the flotation feed.

Figure 2.1 below shows the basic overall process. Flotation is better understood and studied when the process is divided into a number of distinct stages or sub-processes. These are described below.



**Figure 2.1 - Basic Schematic of the Flotation Process**

### 2.2.1 Flotation Sub-processes

While all of the stages or sub-processes of flotation occur simultaneously in a flotation cell, they must occur in the correct sequence for any particular mineral particle to float. The basic stages are as follows:

#### 2.2.1.1 Conditioning of the Ore

The ore is first prepared by processes including comminution (crushing and grinding), which is aimed at liberating the valuable mineral and making its surfaces available for attachment to bubbles. The surfaces are then rendered hydrophobic or hydrophilic by chemical treatment. Typically the valuable or desired mineral is made hydrophobic, using a collector<sup>1</sup>, while the gangue is unaltered or made hydrophilic, with the use of a depressant. Alterations may also be made to the chemical environment, eg the pH or Eh may be changed. It is this induced difference in hydrophobicity that allows separation by flotation to take place.

This surface preparation for flotation is generically termed *conditioning*. While the term conditioning is widely used, there is no concise usable definition for the sub-process. As a result, conditioning has widely varying connotations for experts in different materials processing fields. In its widest definition it can be taken to mean the general preparation of the pulp to be floated, while its most specific meaning might imply one or other particular preparation process.

For the purpose of this study it is necessary to have a precise definition of what is meant by conditioning. As a definition is not available in the literature it is necessary to devise or propose one. This is discussed in detail in section 2.3.

---

<sup>1</sup> Collectors are molecules which have two distinct components: a hydrophobic tail, and a head which is attracted to the mineral surface. Once the head is attached to the mineral surface, the tail extends into the water, creating a hydrophobic surface around the mineral. With depressants, the opposite affect is achieved through a hydrophilic tail.

### 2.2.1.2 Attachment of Mineral Particles to Bubbles

After the ore has been conditioned, the prepared slurry is aerated with fine bubbles. The now hydrophobic mineral particles, on collision with the bubbles, preferentially attach to the bubbles and are lifted out of the bulk slurry to the surface. The flotation of a single particle thus requires a number of steps, namely collision, attachment, and remaining on the bubble all the way to the slurry surface [Kelly and Spottiswood, 1982; Jordan & Spears, 1990]. The overall probability of flotation can be expressed as a product of the probabilities of each of the steps occurring (equation (1)):

$$P_{\text{flotation}} = P_{\text{collision}} \cdot P_{\text{attachment}} \cdot P_{\text{stay}} \quad (1)$$

In this equation,  $P_{\text{attachment}}$  is determined by the hydrophobicity of the mineral and, hence, by the effectiveness of the conditioning stage.

### 2.2.1.3 Froth Formation and Removal

The mineral is removed from the slurry by formation of a froth bed above the pulp. Rising bubbles move into this froth phase, taking with them the hydrophobic mineral particles. A stable froth is usually created with the addition of a chemical frothing agent. The froth is removed as it builds up and, along with it, the concentrated mineral.

The froth phase is a complex topic beyond the scope of this work. It must be understood only in as much as its presence complicates and may mask the observed effects of conditioning. The froth phase strongly influences the value of  $P_{\text{stay}}$  in equation (1).

## 2.3 Definition of Conditioning

The Concise Oxford Dictionary defines the verb *condition* to mean *bring into desired state or condition*. This definition applies and extends to *conditioning* of ores for

flotation. The term is loosely used to describe any preparatory stage prior to flotation. Different systems require conditioning for different purposes: while one mineral may require an oxidative conditioning stage, another may need to have the mineral surface cleaned or reduced by an acid wash.

Some examples of conditioning processes include:

- comminution
- oxidation
- acid leaching
- pre-aeration
- $N_2$  /  $SO_2$  gas treatment
- agitation in the presence of flotation reagents
- reagent addition in the mill
- boiling (to dissolve collector)
- ammonia addition (in chrome flotation)
- pre-grinding (attrition of surface)
- activation
- flocculation
- depression
- pH modification
- acoustic vibration
- split conditioning (prior size classification)
- redox control
- wetting
- bacterial pretreatment

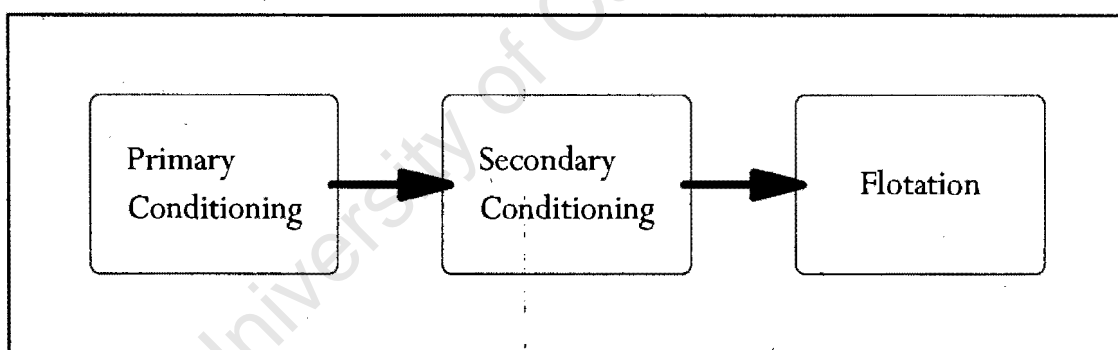
Because of this profusion of processes and their widely varying function, conditioning has different connotations for different operators and researchers. No single definition for conditioning is to be found in the literature. However for the purpose of this project, a usable and precise definition of conditioning is required, both to limit as well as to define the boundaries of the work to be covered. The definition must be able to account for all of the processes already mentioned and yet allow a *conditioning process* to be easily identified as such.

The processes listed above appear to fall into two distinct categories. They are distinguished by their different function and the order in which they typically occur.

The first group relates to the *physical preparation of the surface of the particles*. This includes comminution, oxidation, acid leaching and bacterial pretreatment. The steps usually occur first in the flotation process, preparing the mineral for the second stage of conditioning. Hence this category of processes will be termed primary conditioning. An important point to note is that primary conditioning, with the exception of attritioning, almost always takes place prior to the entry of the pulp into the flotation vessel.

The second category relates to the *process whereby prepared particles are rendered hydrophobic or hydrophilic through mixing, control of the environment and contacting with reagents*. This follows primary conditioning and will be termed secondary conditioning. This process does not change the nature of the mineral surface, but rather results in a change in the charges presented to the surrounding water. This is generally achieved by the adsorption of chemical reagents in a stirred vessel.

Figure 2.2, below, is a schematic of the flotation process as it has now been defined. This represents the sequence of microscopic processes each particle needs to undergo in order to be floated.

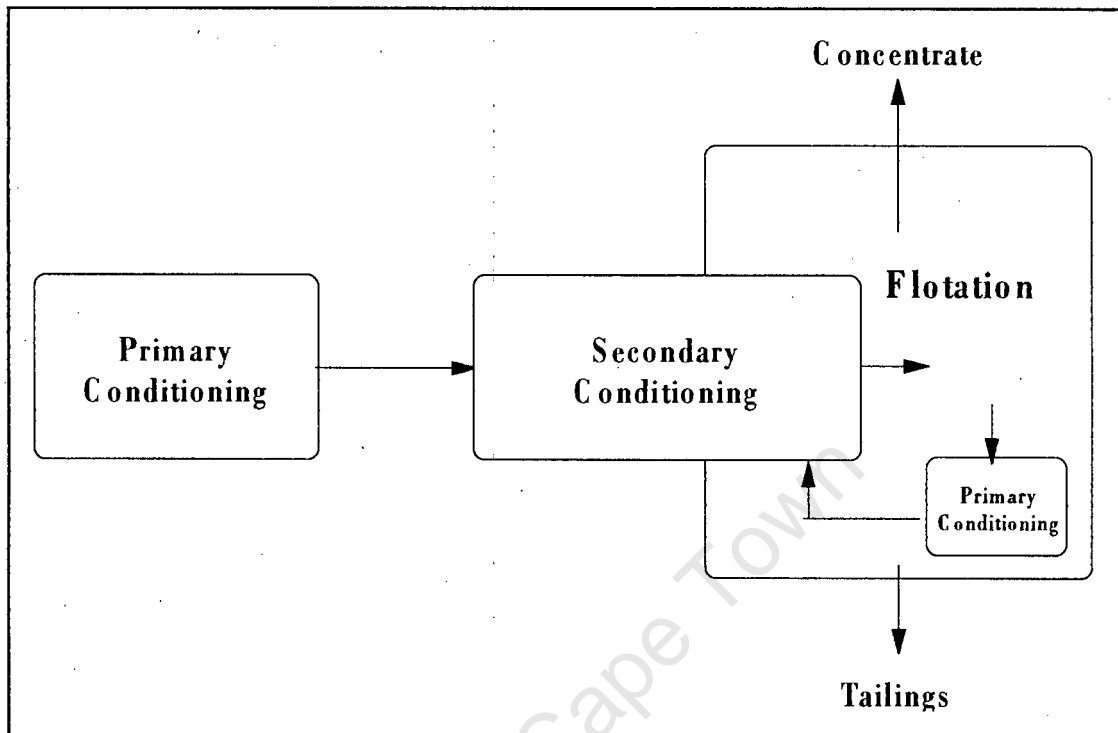


**Figure 2.2 - Schematic of Flotation Showing Conditioning**

Secondary conditioning, defined above as a *process of mixing and contacting with reagents*, can be carried out in a separate vessel (the conditioning tank). It can, however, also occur in the flotation vessel - even during aeration and flotation. This is because agitation is continued during flotation in conventional sub-aeration cells<sup>2</sup>. So although, on a micro scale, each particle experiences the above sequence of processes, on a macro scale the process is more correctly defined as shown below in Figure 2.3. Some attritioning and perhaps even leaching and oxidation may also occur

<sup>2</sup> Agitation does not continue in column cells, which is the basis of Von Holt's work [1992]. In this case, the effectiveness of the conditioning stage prior to flotation is particularly important.

on a small scale in the flotation vessel during flotation, hence the reappearance of primary conditioning (to a limited extent) in the flotation stage.



**Figure 2.3 - Macro-Scale Representation of Conditioning**

Having thus defined conditioning, it is possible to isolate the aspect of conditioning to be studied in this work. Primary conditioning is by its nature system dependent, while secondary conditioning involves the more universal process of mixing in the presence of reagents to alter hydrophobicity. For this reason secondary conditioning will be considered. The specific aspect of secondary conditioning to be investigated is:

*The mixing of prepared particles with collector with the aim of achieving contact and successful attachment or adsorption of collector onto the desired mineral, thereby rendering the surface hydrophobic for flotation.*

The variables which affect this aspect of conditioning, and the influence they have on conditioning efficiency, are identified in section 2.5 below. First, however, it is important to understand the structure of collectors, since they perform a vital role in altering the surface chemistry.



## 2.4 The Structure of Collectors

Collectors are traditionally ionic molecules. This enables them to selectively attach to the charged mineral surface. As previously stated, they also have hydrophobic (typically hydrocarbon) tails, which extend into the water to increase the hydrophobicity of the mineral-collector complex. The hydrophobicity arises from the non-polar nature of the tail.

Owing to their chemical properties and hydrophobicity, collectors have a number of interesting nuances. One of the most important is the formation of micelles. This phenomenon occurs when collector is added in great excess. The hydrophobic nature of the tails causes them to clump together, squeezing out the water. This leads to clumps of insoluble collector forming, which are relatively immobile and do not attach to the mineral surface effectively; thus collector is wasted. But worse than that is the formation of micelles on the mineral surface, where the hydrophobic tails of the first layer of collectors are shielded by the next layer of collector. This reduces the hydrophobicity of the mineral, and hence the floatability. It is evident that there is an optimum collector addition, which is less than the amount which results in micelle formation (critical concentration of micellation).

The extent of collector adsorption onto the mineral surface is determined by the equilibrium between collector in solution and surface collector. Figure 2.4 shows how the concentration of the collector in solution relates to the surface conditions. Initially, individual collector molecules attach to the mineral surface (A). There is plenty of available mineral surface, and adsorption occurs readily. As collector addition increases, adsorption increases, and collector molecules squeeze together, their hydrophobic tails interacting to increase the stability of the adsorbed collector (B). This hydrophobic interaction is termed hemi-micelle formation. Eventually, the surface is so covered by collector that the surface charges are neutralised, and available adsorption sites are scarce. Adsorption removes less of the added collector, until a point is reached where the surface cannot accept any more collector (C). This is the point of mono-layer coverage. Any increase in collector addition results in no additional adsorption, until so much collector is added that the critical concentration of micellation is reached (D). Above this dosage, adsorption increases rapidly as collector particles are attracted to those on the surface by hydrophobic interaction. Since hydrophobicity decreases when multi-layer adsorption occurs, optimum flotation is expected to be found in the dosages between (C) and (D).

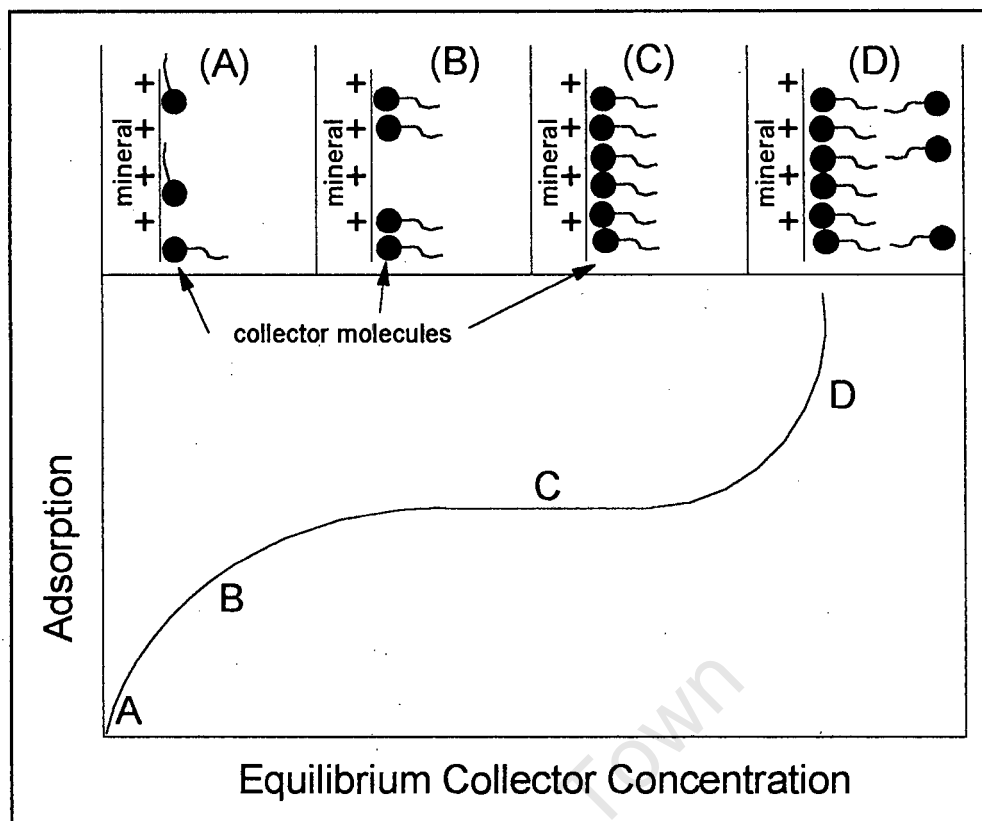


Figure 2.4 - Relationship Between Collector in Solution and on the Surface

The attachment mechanism of the collector onto the mineral surface strongly affects its selectivity and its effectiveness. Since most collectors are ionic, these will be studied briefly to gain an understanding of their mechanism.

### 2.4.1 Anionic Collectors

These are the most widely used collectors in mineral flotation, of which the most common are the sulphidryl or thiol collectors. They are very powerful and selective in the flotation of sulphide minerals. The most widely used thiol collectors are the xanthates (dithiocarbonates). Figure 2.5 shows the structure of ethyl xanthate.

The reaction between sulphide minerals and sulphidryl collectors is complex. Xanthates are assumed to adsorb on sulphide mineral surfaces due to chemical forces between the polar group and the surface, resulting in weakly soluble metal xanthates or insoluble dixanthogen, which are strongly hydrophobic [Wills, 1988, pp 468-470]. Xanthate ions exist as an equilibrium of a number of states, as shown in Figure 2.6. The strength of attachment to the mineral surface is dependent on the degree to which the charge can be rearranged on

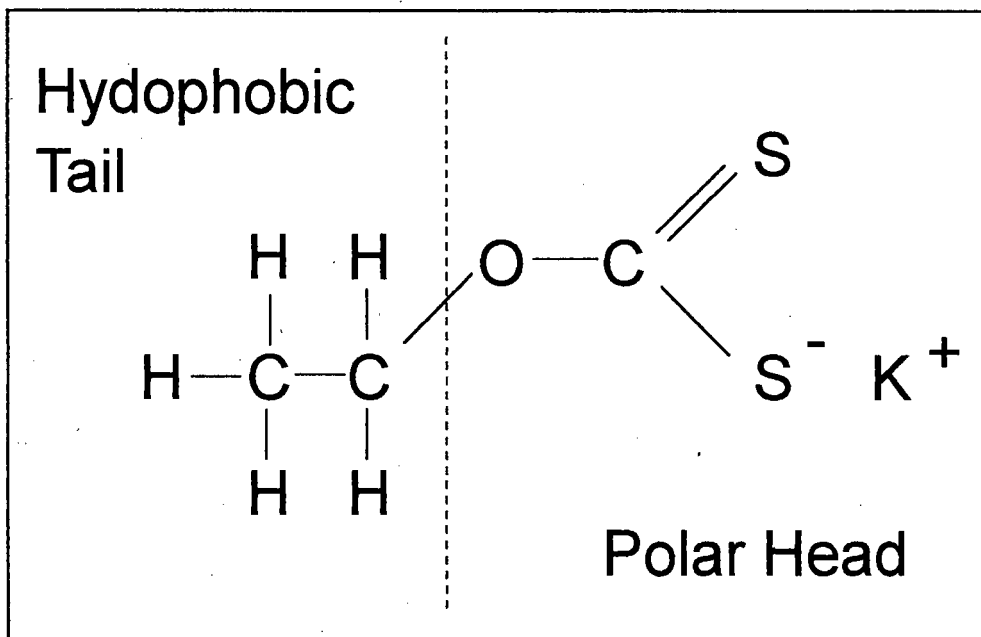
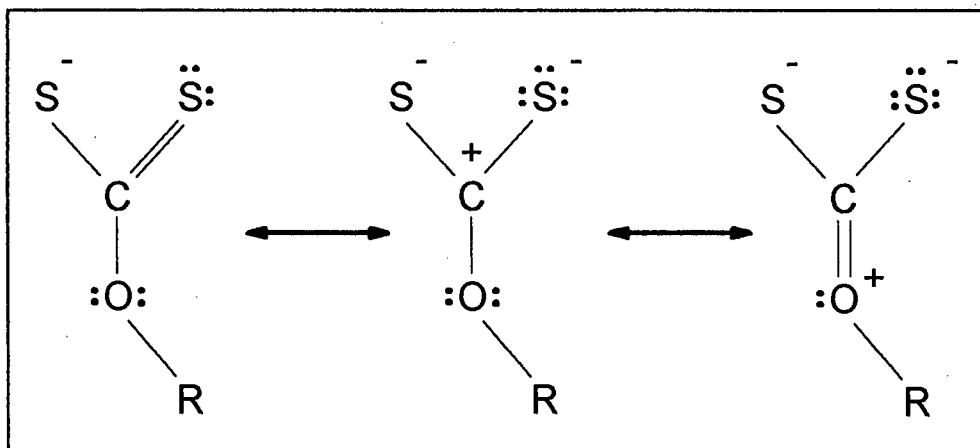


Figure 2.5 - Structure of Potassium Ethyl Xanthate

the collector. The collector may even donate an electron to the mineral. Thus a strong bond between collector and mineral is achieved. Typically thiol collectors chemisorb onto the mineral surface.

#### 2.4.2. Cationic Collectors

The characteristic property of this group of collectors is that the water repulsion is produced by the hydrocarbon group in the cation, where the polar group is based on pentavalent nitrogen [Wills, 1988]. These are amine molecules. Amines are classified as primary, secondary, tertiary and quaternary, depending on the number of hydrocarbon radicals attached to the central nitrogen atom. The primary, secondary and tertiary amines are weak bases and their ionisation is pH dependent. In contrast, the quaternary amines and the alkyl pyridinium salts are strong bases and are completely ionised at all values of pH [King, 1982]. The hydrocarbon chain lengths strongly affect the hydrophobicity of the collector, and hence the effectiveness. Increasing chain length results in increased hydrophobicity. Increased chain length, however, reduces the critical concentration of micellation. This requires a compromise between increasing hydrophobicity and reducing micellation. Typical chain lengths for amine collectors are between 10 and 20 carbon atoms.



**Figure 2.6** - The Electronic States of a Xanthate

Unlike the xanthates, the amines are considered to adsorb on mineral surfaces primarily due to electrostatic attraction between the polar head of the collector and the charged mineral surface. Such forces are not as strong as the chemical forces characteristic of anionic collectors, so these collectors tend to be relatively weak in collecting power [Wills, 1988, p 470]. The electrostatic nature of these collectors makes them less selective. Cationic collectors are used for the flotation of oxides, carbonates, silicates and alkali earth metals.

## 2.5. Stages in Conditioning

Since (secondary) conditioning has been defined above as the process of altering the hydrophobicity of mineral surfaces, it is important to understand the physico-chemical processes leading to increased or reduced hydrophobicity. It has already been shown how the structure of collectors increases hydrophobicity of the mineral particles. Figure 2.7 and Figure 2.8 below show how hydrophilic minerals adsorb the collector molecules, rendering the particles hydrophobic.

This mineral is hydrophilic because the free ions available at the surface allow attachment to polar water molecules and hence the mineral is wetted (Figure 2.7).

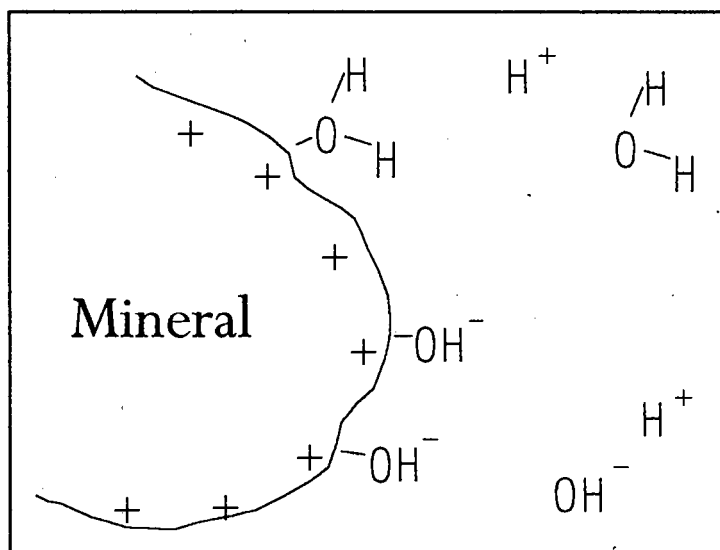


Figure 2.7 - Hydrophilic Mineral

Water molecules at the mineral surface have now been displaced by the collector molecules (Figure 2.8), which, having hydrophobic tails projecting away from the mineral surface, render the mineral surface more hydrophobic.

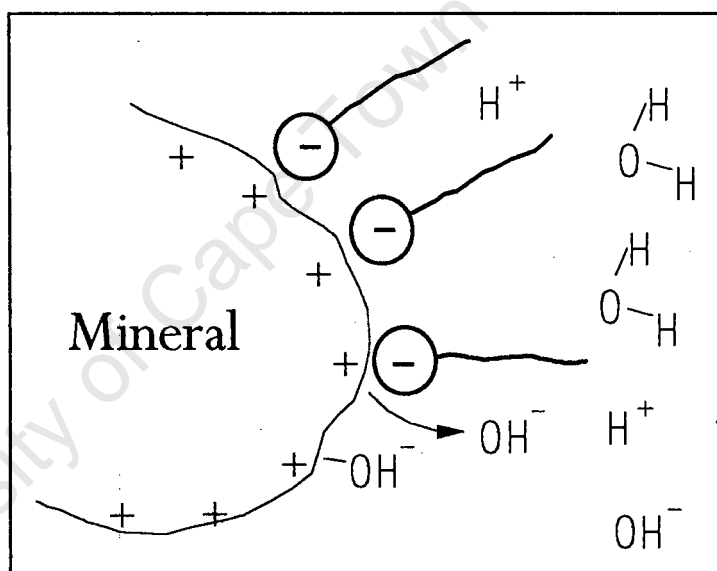


Figure 2.8 - Mineral Is Made Hydrophobic

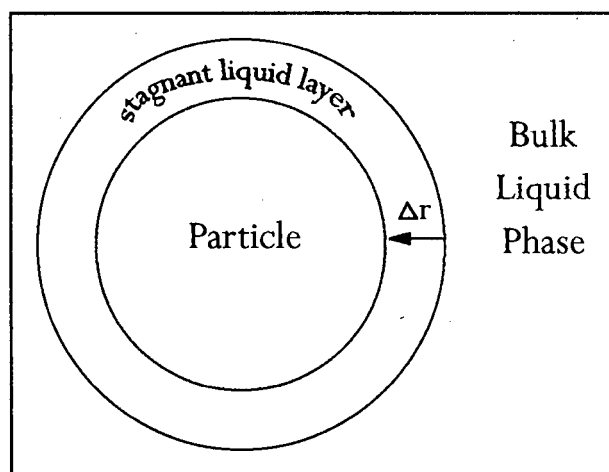
The adsorption of collector onto the mineral surface involves two micro processes, diffusion to the mineral surface and displacement (by the collector) of water. These are discussed in sections 2.5.1 and 2.5.2 below.

### 2.5.1. Diffusion to the mineral surface

This process is illustrated in Figure 2.9. Collector molecules diffuse out of the bulk phase, through the stagnant liquid film around the mineral particle to the particle surface. The distance the collector must travel is  $\Delta r$  and the difference in collector concentration between the surface and the bulk liquid is  $\Delta c$ . Thus the concentration gradient is  $\Delta c / \Delta r$ . This provides the driving force of the

collector toward the particle surface.

The rate of diffusion is proportional to the concentration gradient. Thus the rate of diffusion of the collector to the mineral surface can be increased in two ways, either by increasing the bulk concentration of



**Figure 2.9** - Liquid Phases Surrounding Particle

collector in the liquid, or by reducing  $\Delta r$  (by, for example, increased turbulence in the vessel). If this stage is the limiting factor in adsorption, then the adsorption rate is said to be diffusion or mass transfer controlling.

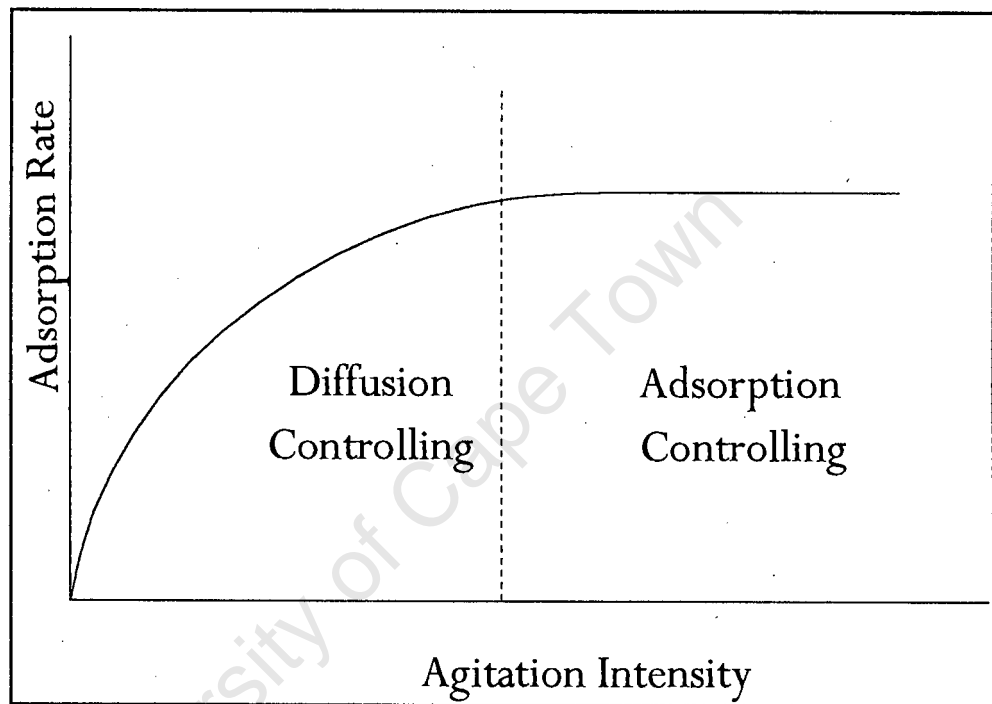
### 2.5.2 Displacement of water

This is determined by the energy required by the collector to displace the water at the mineral surface, and is affected by polarity and the strength of bonds. This factor is largely determined by pH, surface chemistry and temperature. If this stage is the limiting factor in adsorption, then the adsorption rate is said to be reaction or adsorption controlling.

In practice (secondary) conditioning is usually carried out in an open, agitated vessel, through which the pulp flows continuously, and to which measured quantities of reagent (i.e. collector) are added (also continuously). In chemical engineering terms, this is nothing more than a heterogenous stirred tank reactor (STR); thus the theory of STR's applies also to conditioning. This theory is to be found in any standard chemical reaction engineering undergraduate textbook, eg Smith and Van Ness [1987].

According to heterogenous STR theory, the most important factor in determining which variables of conditioning will have the greatest effect in any system is whether the process is mass transfer controlling or adsorption controlling. Figure 2.10 shows how this is typically related to the level of agitation in the conditioning vessel. This figure shows that initially, with low agitation, rate of adsorption is poor (rate of adsorption

is measured in grams or millimoles of collector adsorbed per unit time per unit mass of mineral). This is because the stagnant layer is large and hence slow diffusion to the surface severely limits adsorption rate. As agitation increases so the stagnant layer is reduced and the rate of adsorption rapidly increases. Eventually, a stage is reached when the diffusion to the surface is very rapid and any available collector adsorbing to the mineral surface is immediately replaced by collector from the bulk solution. The adsorption process has become reaction rate controlling and no further increase in agitation can increase adsorption rate.



**Figure 2.10** Adsorption Rate vs Agitation

Agitation is probably the most important single variable affecting (secondary) conditioning. Besides agitation, the following variables are expected to be important in determining the rate and extent of adsorption of collector onto the mineral surface. These are again taken from classical solid-fluid STR theory:

ORE :	Mineral type and degree of liberation Grind size, affecting such features as surface/volume ratio Pulp density
COLLECTOR :	Type, including solubility, polarity and molecule size Dosage Attachment mechanism (eg, physisorption, chemisorption)

SYSTEM :	pH
	Time
	Mixing (power and turbulence)
	Method of agitation (turbulence distribution)
	Temperature
	Ionic Strength

The following section discusses the effect of these variables on conditioning and flotation in some detail.

## 2.6 Thermodynamics and Kinetics of Conditioning and Flotation

This section describes how the above factors affect the rate and extent of adsorption and flotation, by analysing the thermodynamic and kinetic implications of these variables.

Chemical thermodynamics can predict whether a reaction will proceed under a given set of conditions of temperature and pressure. It can also predict the direction in which the equilibrium will be shifted in response to variations in these parameters. At the same time, all chemical reactions are functions of time, and thermodynamics cannot explain the *rate* of reaction nor how rate will vary with temperature, pressure and composition. Only chemical kinetics can provide such information. For flotation this rate is all important, since the economic viability of a process is frequently determined by residence time considerations.

### 2.6.1 Thermodynamic Criterion for Conditioning

Chemical thermodynamics allows prediction of whether a particle can attach to a bubble and be floated. This is done by analysis of the Gibbs free energy change of the system: the overall free energy change must be negative for the attachment to proceed. This is mathematically represented in equation (2):

$$\Delta G = \gamma_{LV}(\cos \theta - 1) < 0 \quad (2)$$

where  $\Delta G$  = Gibbs free energy  
 $\gamma_{LV}$  = liquid-vapour interfacial tension



$\theta$  = contact angle of bubble on mineral surface

This indicates that for flotation to be possible the contact angle,  $\theta$ , must be  $>0$ . The contact angle of a mineral is the classic measure of its hydrophobicity. Thus the more negative  $\Delta G$  the greater the tendency for the particle to dewet. It is important to note, though, that this cannot be used to imply anything about the rate (kinetics) of flotation.

For most flotation systems the following free energy vs distance diagram applies to the approach of a bubble to a mineral surface (Figure 2.11).

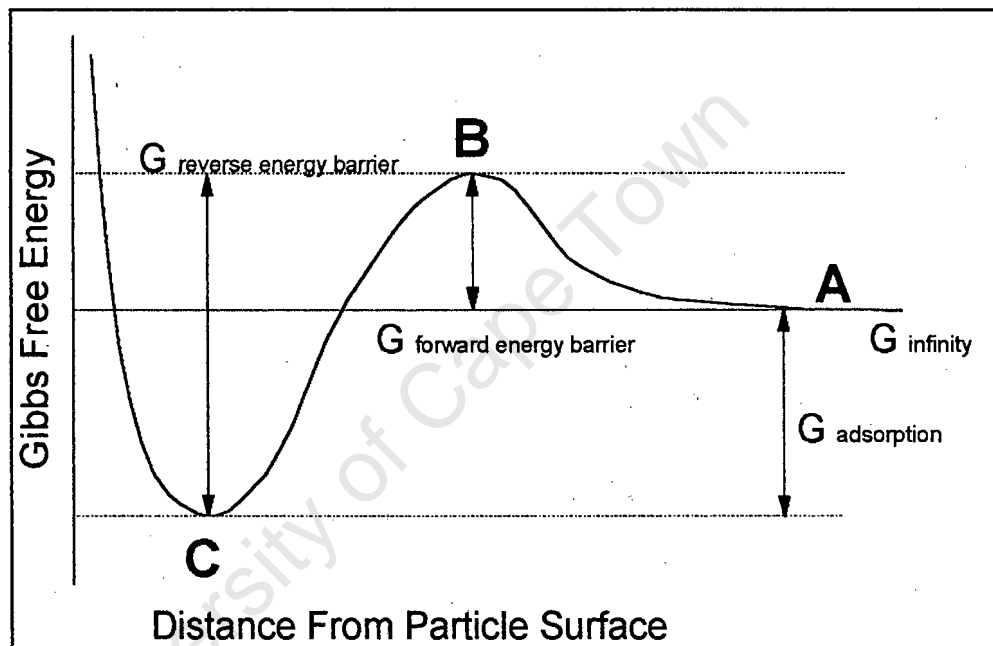
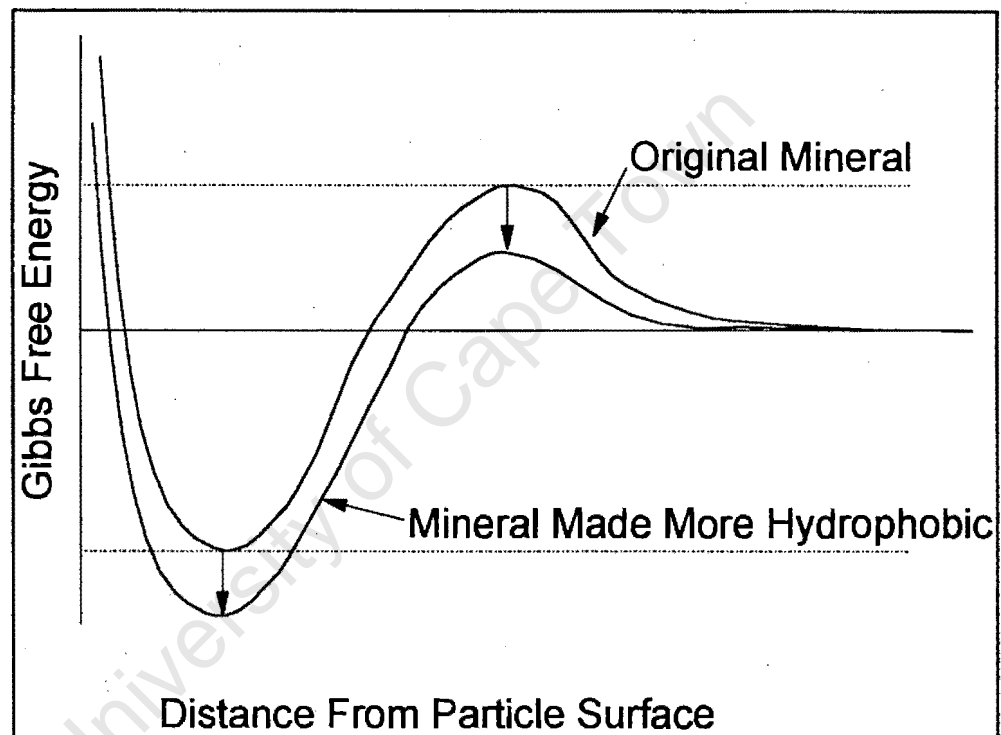


Figure 2.11 - Free Energy vs Distance From Particle Surface

Beyond point A there is no net force between particle and bubble, but on closer approach, there is a net repulsion as Gibbs free energy of the system increases.  $G$  is a maximum at point B and  $\Delta G = B - A$  is the work required to reach B and hence overcome the resistance to attachment. As the bubble and the particle continue to approach each other, free energy is reduced, until C is reached. Thus C is the natural rest distance between the particle and bubble. If the two collide and reach distance C from one another,  $\Delta G$  is negative and they will have attached. While overall free energy change shows the stability and likelihood of the attachment, the forward and reverse energy barriers are significant in indicating the resistance to attachment and detachment and, hence, the probable kinetics of the system.

Thus the aim of conditioning must be to prepare the mineral surface in such a way as to encourage the forward reaction (attachment) and discourage the reverse reaction (detachment). This would have the effect of increasing flotation rate and reducing fall back of particles in turbulent zones (i.e. increasing  $P_{stay}$  in equation (1), section 2.2.1). Laskowski [1993] has shown that, all else being equal, increasing hydrophobicity shifts the energy diagram lower, as seen in Figure 2.12. This has the effect of reducing the total Gibbs free energy change of the system, hence increasing the favourability of attachment, as well as lowering the forward energy barrier and hence increasing the flotation rate.



**Figure 2.12** - Effect of Hydrophobicity on Free Energy Changes

The variables which affect the thermodynamic favourability of flotation include: the extent of mineral liberation (increased mineral surface for collector attachment), collector hydrophobicity and affinity of collector to the mineral (both of which alter surface forces) and pulp temperature (which shifts reaction equilibria).

### 2.6.2 Kinetic Criterion for Conditioning

As was discussed in section 2.2.1.2 flotation can be expressed as a product of the probabilities of the various essential mechanisms occurring. The probability of flotation occurring within a specified time is in fact the overall rate of flotation when multiplied over the numerous particles and bubbles of a real system. Thus the kinetics of flotation can be expressed using the equation (1) introduced previously on page 7:

$$P_{flotation} = P_{collision} \cdot P_{attachment} \cdot P_{stay}$$

or

$$P_f = P_c \cdot P_a \cdot P_s \quad (3)$$

$P_c$  is a function of particle and bubble sizes and numbers in a given volume, and is unaffected by conditioning.  $P_a$  on the other hand is strongly dependent on solution and surface chemistry. For attachment to occur, particles must remain in contact for a definite period of time during collision. This period is required for the disjoining layer of water between particle and bubble to thin, be disrupted and finally removed. This period is termed the induction time. The shorter this induction time, the more likely is the particle-to-bubble attachment. Thus  $P_a$  is essentially a function of critical induction time.

From the force-distance diagram (Figure 2.11) it can be seen that attachment probability will be a function of the forward energy barrier ( $G_{attach}$ ):

$$P_a = f(G_{attach}) \quad (4)$$

This indicates that  $P_a$  is strongly dependant on factors which affect the long-range energy barriers. Hence  $P_a$  is a function of both ionic strength, which reduces the effective distance of the electrical double-layer, and pH, which alters surface charges of both bubbles and mineral surfaces. While the energy

barrier is difficult to measure and no correlation has been found between  $P_a$  and  $G_{attach}$ , this term ( $P_a$ ) does find its way into the more useful concept of induction time.

Eigeles and Volova [1960] performed extensive induction time measurements under varying conditions, such as collector concentrations and temperature. Laskowski [1989] has interpreted their findings to give the following function:

$$\tau_i = \tau_0 \cdot e^{w/kT} \quad (5)$$

where

- $\tau_i$  = induction time
- $\tau_0$  = induction time when kinetic hinderance is a minimum  
i.e. when  $G_{attach} = 0$
- $w$  = apparent activation energy
- $k$  = Boltzmann constant
- $T$  = absolute temperature [K]

Thus induction time, and hence  $P_a$ , is strongly affected by temperature. This was claimed by Kirchberg and Topfer [1964] to be a result of decreased viscosity allowing easier displacement of water at higher temperatures. Dobby and Finch [1987] used the same concept with their assumption that:

$$\tau_i = f(\eta)$$

where  $\eta$  is viscosity.

It is essential that contact time is greater than induction time for the mineral particle to attach to the bubble. Hence for attachment to occur the following statement must hold true:

$$\tau_c > \tau_i \quad (6)$$

where  $\tau_c$  = contact time between mineral particle and bubble

This is termed the kinetic criterion for flotation and must be satisfied along with the thermodynamic criterion of  $\Delta G < 0$ . Furthermore, for all conditions,  $T > 0$ , and hence:

$$\tau_i > \tau_0 \quad (7)$$

So that:

$$\tau_c > \tau_i > \tau_0 \quad (8)$$

From this Laskowski [1989] postulates that possibly:

$$P_a = 1 - \exp \left[ - \left( \frac{\tau_c - \tau_i}{\tau_0} \right) \right] \quad (9)$$

According to this relationship,  $P_a=0$  for  $\tau_c \leq \tau_i$  and  $P_a$  is close to unity when  $\tau_c \gg \tau_i$ .

The development of equation (9) shows how the probability of attachment relates to induction time and contact time, as well as the importance of the concept of the forward energy barrier caused by long range repulsive forces. What this also shows is that the probability of attachment is proportional to temperature and is also a strong function of both pH and ionic strength of solution. It was not however found to be directly related to hydrophobicity. This is because hydrophobicity is a static equilibrium (thermodynamic) measurement of component surface forces, while induction time is a kinetic parameter and relies on aspects of the surface forces relating to the forward energy barrier. Thus while the thermodynamic criterion of  $\Delta G < 0$  is essential for flotation to take place, the total free energy change is less important than other hydrodynamic factors in determining probabilities (rates) of attachment.

Particle and bubble size are also important factors affecting probability of attachment. Induction time is inversely proportional to particle size, owing to the reduced significance of repulsion forces in larger particles, while the contact time available for attachment increases proportionally with bubble size.

Thus conditioning can be seen to play two important roles in flotation thermodynamics and kinetics. The first is in creating a hydrophobic surface to satisfy the thermodynamically necessary criterion of  $\Delta G < 0$ . The second is in

meeting the kinetic criterion of  $\tau_c > \tau_i$ . This is done through reducing the long range repulsion forces by altering the surface charges of the particles, thus improving  $P_a$  and hence flotation kinetics.

Additionally, collectors on mineral surfaces are known to interact with surfactants on bubbles [Leja and Schulman, 1954], thus further improving  $P_a$  and  $P_s$ . The mechanisms involved are poorly understood, but are postulated to involve hydrophobic interaction, which can be represented as shown in Figure 2.13.

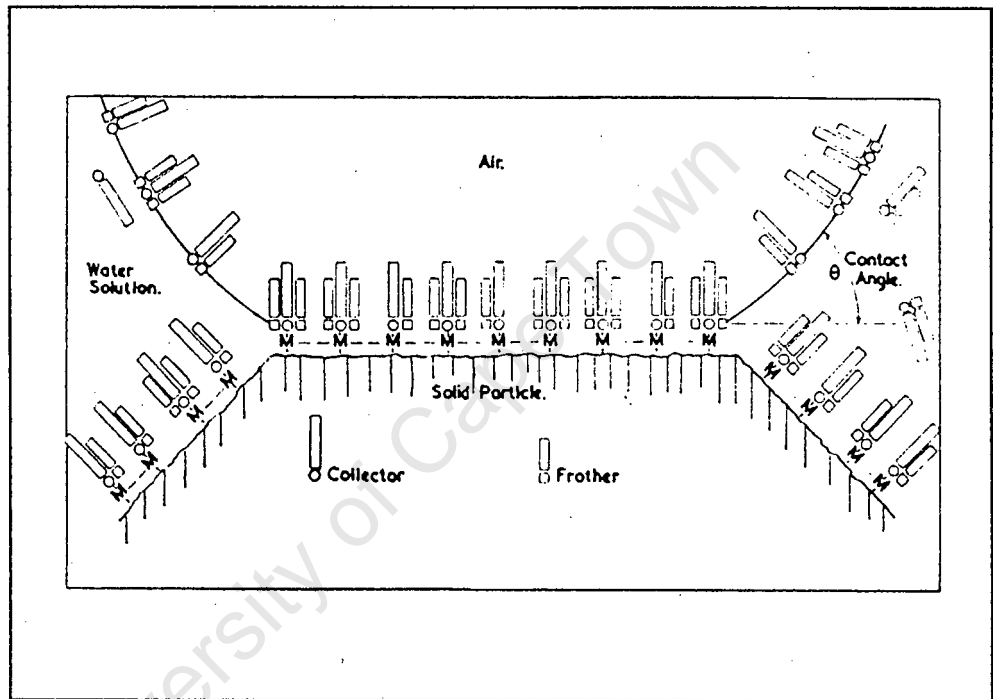


Figure 2.13 - Collector-Surfactant Interaction (from Leja and Schulman, 1954)

## 2.7. Mathematical Modelling of Flotation - The Klimpel Flotation Model

The Klimpel flotation model, so named after Dr R.R. Klimpel, is a widely accepted means of describing the rate of flotation of a mineral for any given system. This model is a regression model, which aids in expressing differences between flotation systems, but cannot be used to predict flotation rate or recovery in any given system. Its fundamental basis lies in combining flotation kinetics with pulp density functions, integrated over time, to give recovery curves. The equation for the model is shown in equation (10) below:

$$\text{Recovery} = R \left[ 1 - \frac{e^{-kt}}{kt} \right] \quad (10)$$

where  $R$  = ultimate (final or equilibrium) recovery

$k$  = initial rate of recovery

$t$  = time

The best way to understand how this function may be used is by looking at an example provided by Klimpel [1984]. Figure 2.14 below shows two flotation yield - time curves for a copper-xanthate system. A low collector dosage of 22.3 g/ton results in a low initial flotation rate but high ultimate recovery, while a high dosage of 63.2 g/ton has a higher initial flotation rate but lower ultimate recovery. The Klimpel model fitted to these curves, yields the Klimpel  $R$  and  $k$  values given in Table 1, below.

Table 1: Klimpel Values for Copper Flotation at two Collector Doses

Collector Dosage	Klimpel $k$	Klimpel $R$
22.3 g/ton	1.59	0.908
63.2 g/ton	0.90	0.999

Figure 2.14, is a typical example of a trade-off between the kinetic and the thermodynamic effects in flotation and has been described as the  $R/k$  trade-off. Initially flotation is kinetically controlled, while the ultimate recovery is determined by the thermodynamics of the system.

In an industrial application, the duration allowed for flotation would determine which of the two recovery curves would be favoured for recovering a given mineral. The cross-over point determines the time beyond which the equilibrium or  $R$  value becomes more important than the rate or  $k$  value. Ideally conditioning should result in increases in both  $k$  (rate) and  $R$  (equilibrium) values. If this happens, it will have the effect on the recovery (yield) - time profile shown in Figure 2.15.

While the Klimpel flotation model is useful in describing recovery curves, it must be remembered that it is a great simplification of the mechanisms in action. Particularly it assumes that all particles remain exactly as floatable as they were when flotation

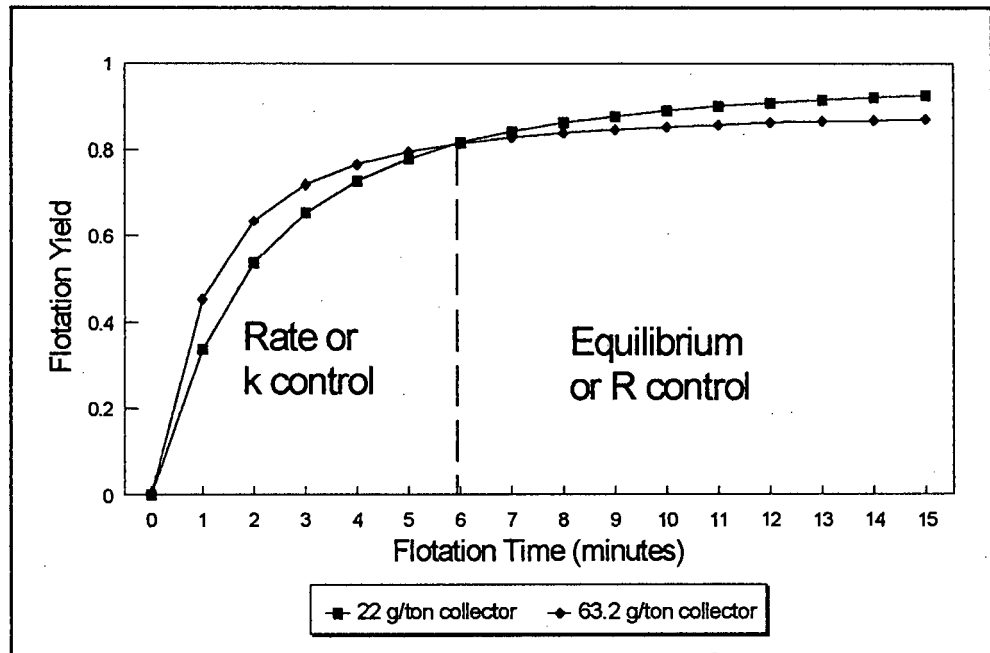


Figure 2.14 - Relative Importance of Klimpel  $k$  and  $R$  Parameters

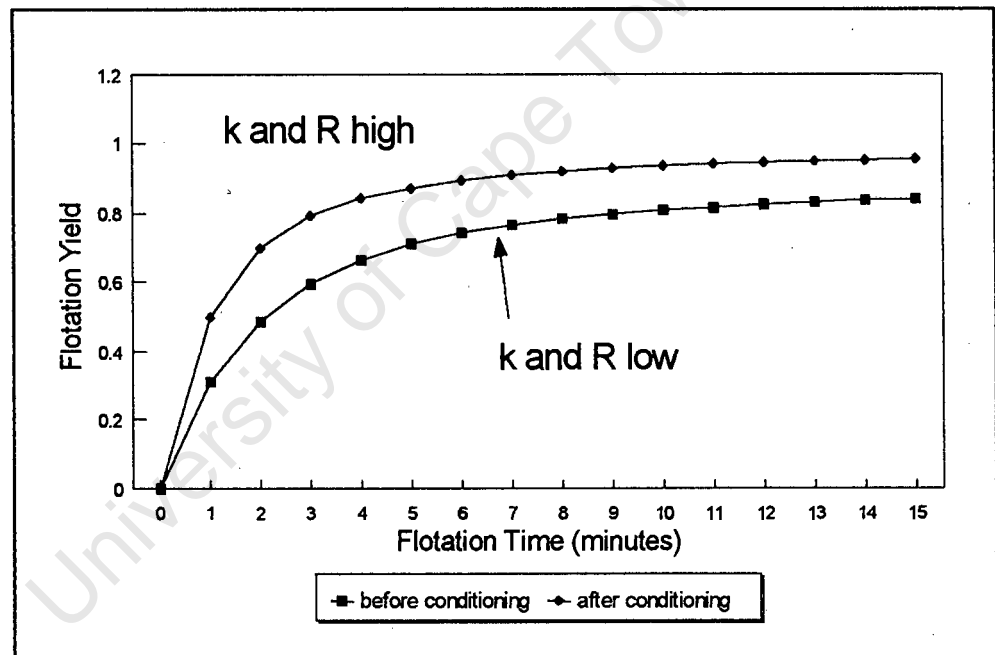


Figure 2.15 - Effects of Increased  $k$  and  $R$  Values on Recovery (Yield)

began. This is a poor assumption, since secondary conditioning is known to continue during flotation.

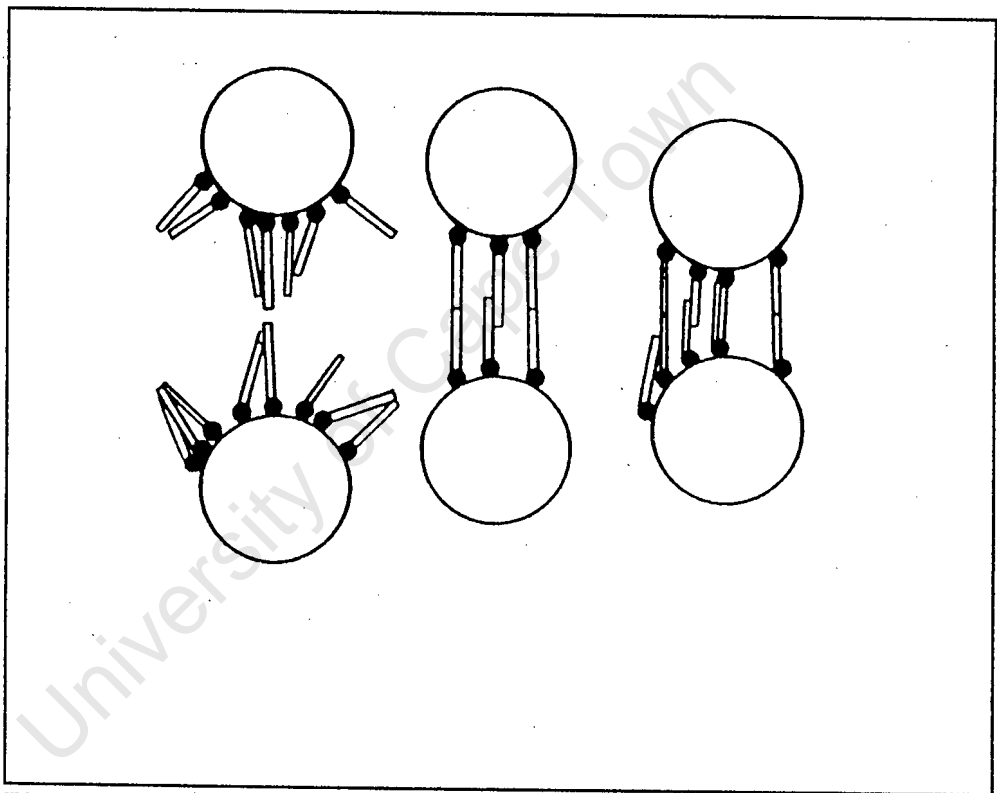
## 2.8 Shear-flocculation

Shear-flocculation refers to the observed flocculation which can occur in highly agitated systems. The effect of shear flocculation is to change the apparent particle size



distribution in the pulp. As is shown in section 2.9.2 below, particle size is one of the most important factors affecting flotation performance. Thus shear-flocculation can have a strong influence on the flotation of a mineral.

In shear-flocculation, the energy barrier resulting in repulsion of similarly charged hydrophobic particles is overcome by intense mixing [Subrahmanyam and Forssberg, 1990; Shouci and Song, 1991]. The formation of hydrophobic aggregates results from the fact that the hydrophobic interaction energy is a few hundred times greater than the energy of molecular or electrostatic repulsion. This type of aggregation is favoured when the mineral is coated with collector molecules of long chain length. The hydrophobic interaction is shown in Figure 2.16 below.



**Figure 2.16 -** Hydrophobic Interaction of Shear-Flocculated Particles  
[Shouci and Song, 1991]

Shear-flocculation can be induced during conditioning by using very high impeller speeds. There is a cut-off speed below which agitation merely facilitates mixing and diffusion of reagents. If this speed is exceeded, shear-flocculation takes place and greatly complicates the conditioning sub-process.

Shear-flocculation can have particular relevance in the flotation of ultra-fine particles. These can be removed from the system by a technique termed carrier flotation, where

a few large particles act as sites for attachment of the ultra-fines. The attached fines are then floated as part of a larger conglomerate. The optimum sizes and ratios of fine to large particles can be calculated from collision theories.

## 2.9 Research in Conditioning

Large volumes of literature can be found on almost every variable of flotation. Much of this work is largely empirical and very system specific. However, there is no work which tries to define conditioning in a global sense. Most conditioning work centres on specific preparation problems. Additionally the design of conditioners has received little attention, with retention time and the agitation required to keep the particles in suspension being the two factors chiefly considered. It is only recently that interest has been shown in the mechanics of conditioners and the effects of conditioning intensity and turbulence on flotation recovery and grade. An overview of the more general expositions on variables of conditioning, and in what direction conditioning studies are moving, is given in this section.

The effect of the duration of conditioning on flotation has been acknowledged in some of the earliest works including that of Wark and Sutherland [1955]. But the first in depth investigation into the possible affect of the *power input* into the conditioning stage was made by Rubio [1978]. His results showed that the grade of flotation concentrate of copper minerals was increased with increasing energy in the conditioning stage.

Duchen [1980a, 1980b, 1982] showed similar findings for conditioning of ore bearing Au,  $U_3O_8$  and pyrite. His first work discusses the effect of the *type of agitation* used in conditioning on the flotation of Witwatersrand pyritic ore. His results showed that high intensity mechanical agitation provided better initial rates of recovery, at far superior grades, than occurred as a result of agitation through aeration. This improvement in rate and grades was greatest for high impeller speeds. This work was extended to investigate the effect of *intensity of agitation*, with impeller speeds ranging from 700 rpm to 2 100 rpm, representing a 27 fold increase in power input. Figure 2.17 shows the effect of impeller speed on rate of recovery, expressed as first order rate constant  $k$ , for gold, uranium and pyrite. In all cases grade of mineral recovery increased with increasing impeller speed. Figure 2.18 shows the effect of impeller speed on equilibrium recovery, expressed as a percentage of mineral in the

feed. The figure shows that increased impeller speed resulted in increased equilibrium recovery for gold and pyrite; the response of uranium was more complex.

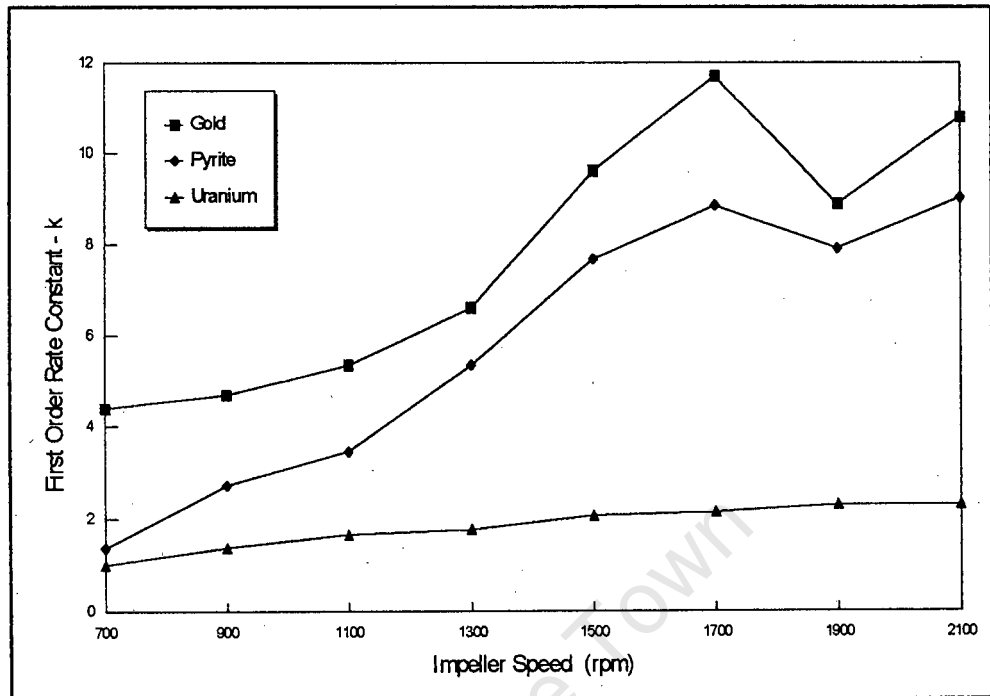


Figure 2.17 - Effect of Impeller Speed on Rate of Flotation [Duchen, 1980]

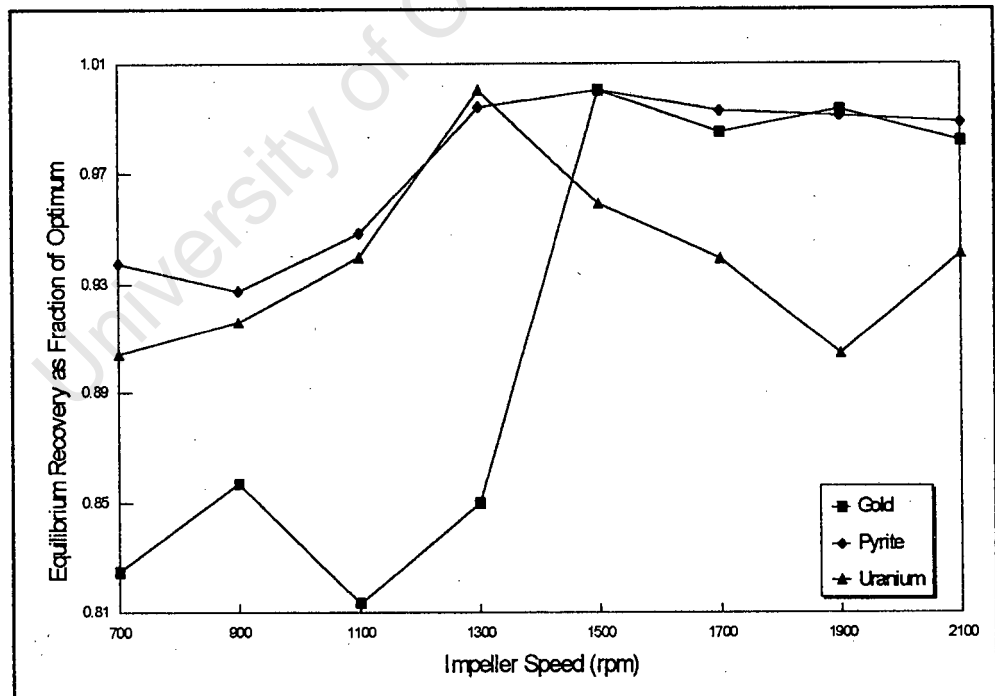


Figure 2.18 - Effect of Impeller Speed on Equilibrium Recovery [Duchen, 1980]

Later work by Duchen [1982] investigated the effects of *extended conditioning time* on froth flotation of gold, uranium and pyrite from the same ore as previously used.

Again, mechanical conditioning greatly improved flotation rate and grade. The improvement with respect to conditioning time was observed to improve to a peak and then fall off for extended durations, in the region of 1 hour.

More recently, it has been found that the selectivity and recovery of fine particles can be much enhanced by *increased energy input* in conditioning. This is shown in work carried out by Bulatovic and Salter [1989], where finely ground complex copper ores were subjected to varying power input ( $0.4 \text{ kW/m}^3$  of pulp) in the conditioning stage.

Anderson [1988] studied the flotation of coal using oily collectors. His study of various oils revealed that "with any one oil, conditioning procedures were found to have a marked influence on flotation performance". His work showed that conditioning the coal with collector in a small volume (hence *high intensity of mixing*) before adding water to dilute the pulp for flotation often produced far superior results. "The most common way of introducing oil in batch flotation experiments (where the cell is full so that agitation conditions are comparatively mild) generally produced poorer grades". Interpretation of his work is complicated, however, by the need to disperse the oil into fine droplets before they attach onto the coal particles.

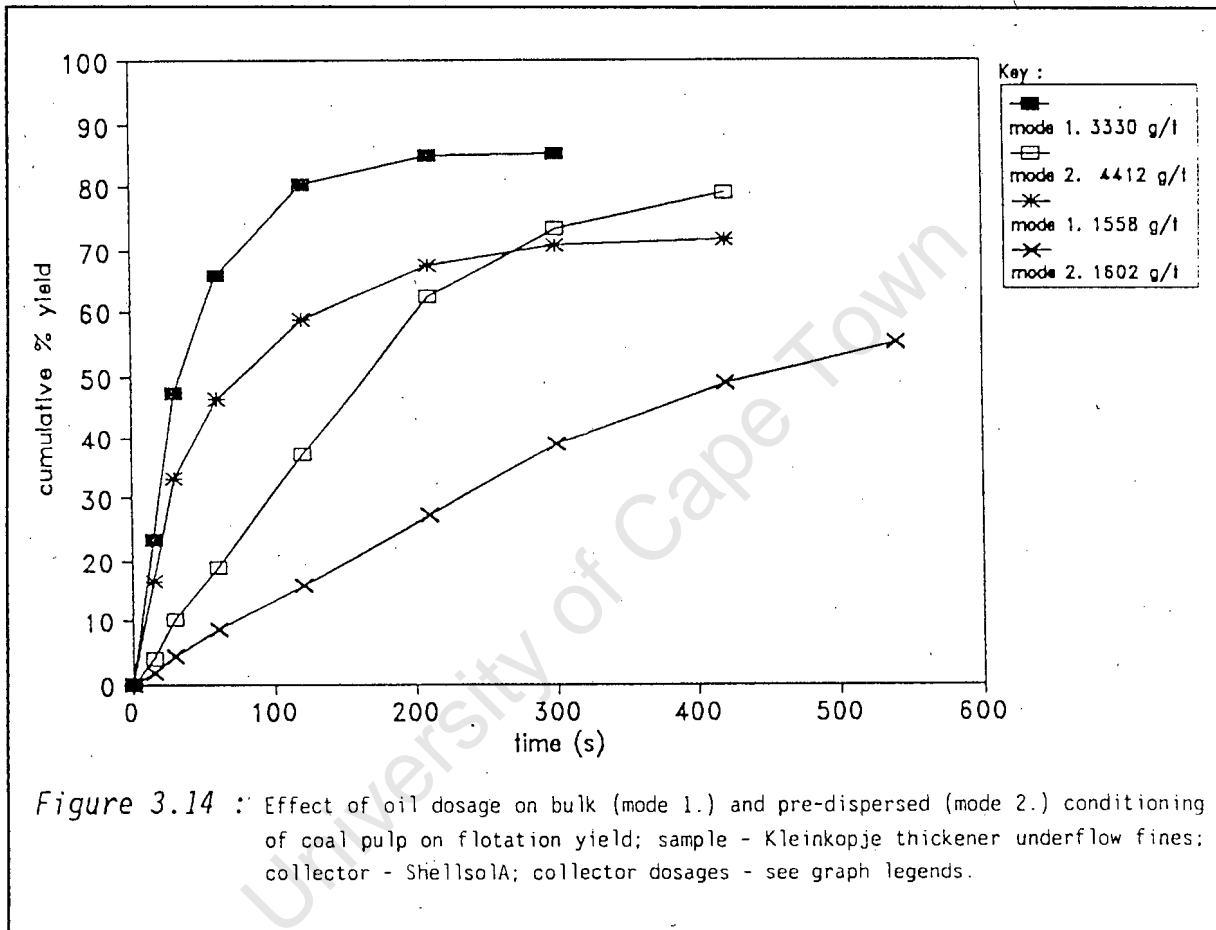
The most recent work covering the concept of power and energy in the conditioning stage is that of Stassen [1990, 1991a, 1991b], using South African  $\text{U}_3\text{O}_8$  and pyrite ores. His complete work including experimental procedure, captured data and development of equations and conclusions has been obtained in thesis form, and is more fully analyzed in the next sub-section (2.9.1) and in Chapter 3 below.

Von Holt [1992] studied the column flotation of coal. His work highlights the importance of conditioning prior to flotation. The column cell is a quiescent flotation system. This means that while batch or other agitated cells input a high level of energy into the slurry (often eliminating or reducing the need for a separate conditioning stage), little energy is input during column flotation. The problems associated with poor conditioning are thus magnified in column flotation. Von Holt showed that the method of conditioning strongly affected flotation performance. He also identified a number of other conditioning variables which affected flotation performance. The most important variables were as follows:

- Method of Collector (oil) addition
- Impeller Speed
- Cell Type

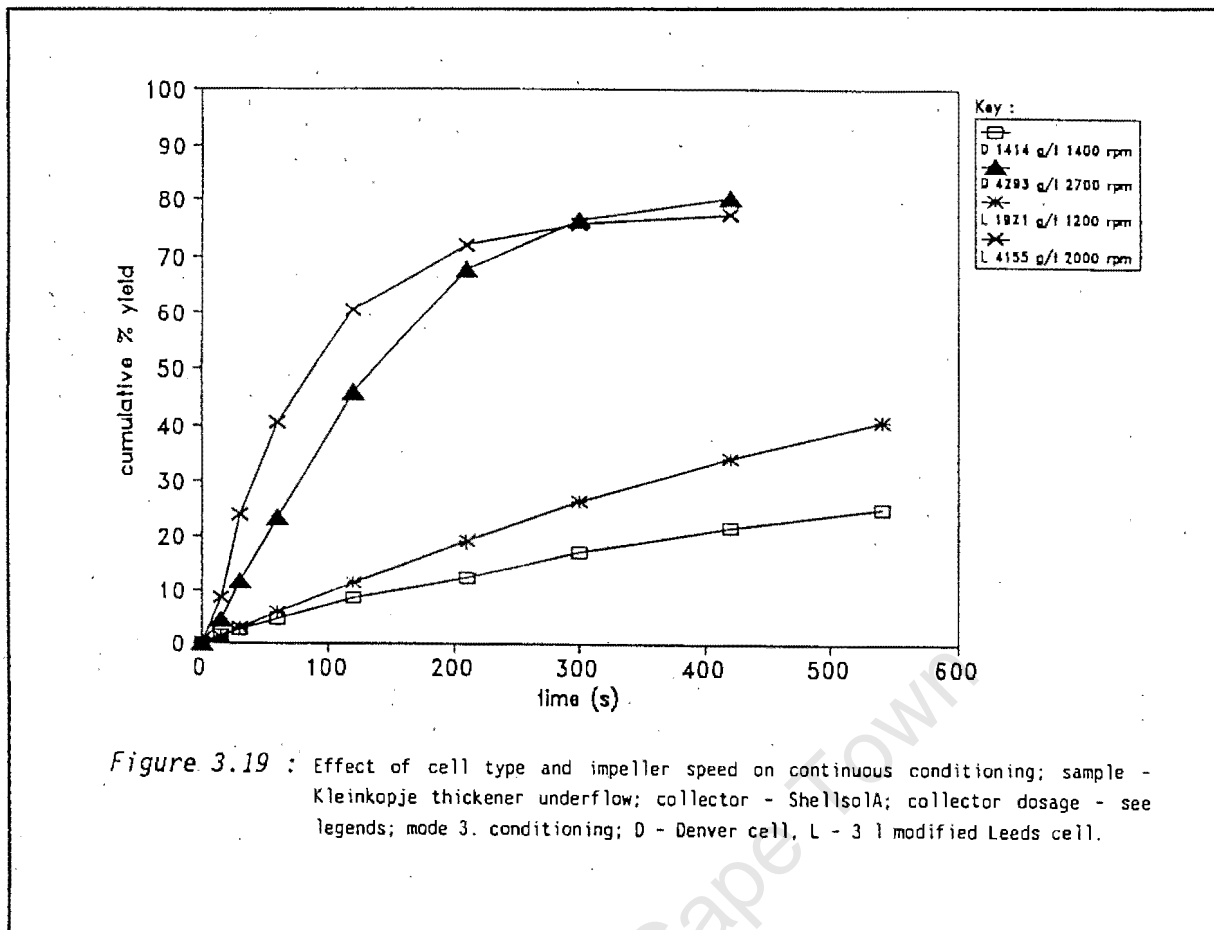
- Collector (oil) dosage
- Scale of Conditioning (relates to turbulence achieved)

While conditioning in coal flotation includes the dispersion of insoluble collector, the results are remarkably similar to those achieved for soluble collectors. Von Holt's work is not a study of conditioning per se and hence the results are largely qualitative, but they show very clearly the differences in response to the above variables. These are shown in Figure 2.19, Figure 2.20 and Figure 2.21.



**Figure 2.19 - Effect of Method of Collector Addition on Flotation Response [Von Holt, 1992]**

Figure 2.19 shows the effect of the method of collector (oil) addition, as well as dosage on flotation response. Addition of the oil as a bulk "slug" (mode 1.) gave the best yields, with the batch addition of the oil as a pre-dispersed oil-water emulsion substantially worse. Further work showed that continuous addition was worse still. This was probably due to additional conditioning in the batch systems. As would be expected, increased collector dosage resulted in increased flotation response. This is shown again in Figure 2.20 below.



**Figure 2.20 -** Effect of Collector Dosage and Impeller Speed on Flotation Response [Von Holt, 1992]

Figure 2.20 shows the effect of collector dosage and impeller speed on flotation performance, using both a Denver (3l laboratory) cell and a Leeds (3l laboratory) cell. Increasing collector dosage and impeller speed increases flotation response, with both cells showing marked improvement in yield when dosage is increased from 1500 g/ton to 4000 g/ton. At both dosages the Leeds cell showed a slight improvement in performance over the Denver cell. The effect of cell type is even more evident, when the 3 l Leeds cell is compared with a 240 l Pilot conditioning tank (Figure 2.21). The use of the Leeds cell for conditioning results in far more rapid flotation response and a higher ultimate yield. Von Holt suggested that this was as a result of a much reduced conditioning turbulence, that of the pilot cell being in the order of one magnitude below that of the Leeds cell.

Jameson and Ralston [1992] point out that in much of the previous work in conditioning, "much emphasis was placed on the energy input into the conditioner. However, the hydrodynamic effects of high shear and intensive agitation are only one part of the phenomenon. The influence of pulp chemistry in high-energy conditioning

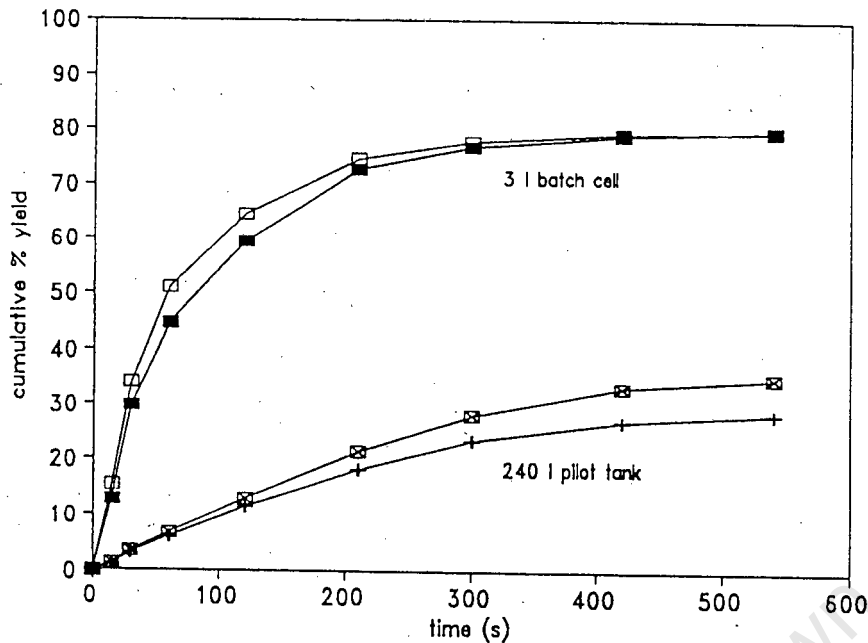


Figure 3.21 : Comparison between bulk addition of oil to a 3 l laboratory Leeds cell (batch cell) and a 240 l capacity pilot rig tank; sample - Kleinkopje thickener underflow fines; collector dosage - nominally 1500 g/t.

Figure 2.21 - Effect of Cell Size on Flotation Response [Von Holt, 1992]

is critical." A joint research proposal prepared by these two authors suggests that mechanisms including cleaning of oxidised surfaces, agglomeration of valuables and dispersion of flocculated gangue particles may be involved in improving recovery in high intensity conditioning systems.

Ralston [Blake and Ralston, 1985; Crawford and Ralston, 1988] has been intimately involved in studying a number of fundamental aspects of flotation relevant to the conditioning stage and related mechanisms. Section 2.9.2 provides an overview of the important variables covered by his work.

### 2.9.1 Stassen

The work of Stassen is concerned with the effect of energy input in the conditioning of ores prior to the flotation stage. His thesis [Stassen, 1990] investigates energy input as a function of conditioning time and impeller speed;

as the following abstract from a subsequent paper on the topic [Stassen, 1991a] shows:

*SYNOPSIS (J.S.A.I.M.M., vol 91, no. 5)*

*The effect of conditioning energy on the flotation of gold,  $U_3O_8$ , and pyrite was investigated in the range 0.1 to 100 kWh per tonne of dry ore for various combinations of conditioning time and impeller speed in a cylindrical conditioning tank. It was found that, when the conditioning energy was increased to between 5 and 10 kWh per tonne of dry ore, the total recovery and flotation rate of the valuable minerals (expressed as Klimpel parameters) increased substantially. The Klimpel parameters are dependent on conditioning energy, but are independent of conditioning time or impeller speed (at constant conditioning energy). The Klimpel parameters of the gangue are independent of conditioning energy.*

The following function was derived to describe the flotation rate and final recovery (as Klimpel parameters) obtained after conditioning in a stirred batch tank system. The Klimpel parameters are represented by  $\Phi$  (The full derivation of the function can be found in Chapter 3 below, together with details of the experimental equipment, technique and results obtained).

$$\Phi = \Phi^{\max} - \Delta \Phi . e^{-K_c (P/V)_c^\gamma t_c} \quad (11)$$

where  $\Phi$  = Klimpel parameters k or R

$\Delta \Phi = \Phi^{\max} - \Phi^{\min}$

K = proportionality constant

P = power input

t = time

V = volume

$\gamma$  = exponent of power

c : subscript referring to conditioning

Results were obtained for a large number of combinations of power and time. The results were then fitted to the function above using least squares regression.



Stassen's data showed that  $\gamma \approx 1$ , and that setting  $\gamma$  for time (initially 1) equal to  $\gamma$  for power gave little loss in statistical accuracy ( $r^2$ ). With  $\gamma_{\text{power}} = \gamma_{\text{time}}$  the function simplifies the P and t terms, reducing them to Energy, giving:

$$\Phi = \Phi^{\max} - \Delta \Phi \cdot e^{-K_c \cdot E_c^\gamma} \quad (12)$$

where  $E = \text{Energy}$

The following charts (Figure 2.22, Figure 2.23 and Figure 2.24) show the experimental results obtained by Stassen. The results are plotted as  $k$  and  $R$  against  $\log \text{Energy}$ , with the regressed function drawn through the points. This work shows that there is a definite relationship between mixing energy and flotation grade and recovery, though the spread of data would indicate a poor fit to the function chosen. The work also implies, from the fact that the power and time terms reduce to energy, that the energy input into the conditioning stage is more critical than the components of power input or duration of mixing.

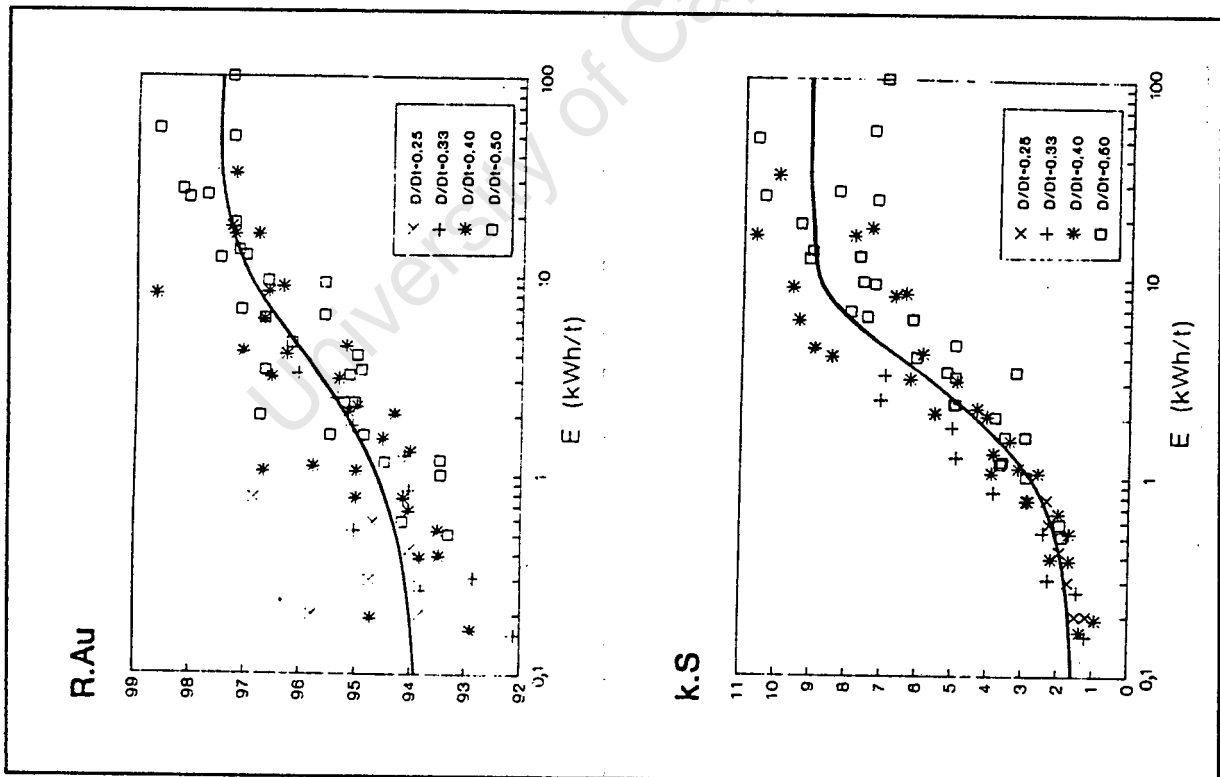


Figure 2.22 - Klimpel Parameters for Sulphur vs Conditioning Energy (from Stassen, 1991a)

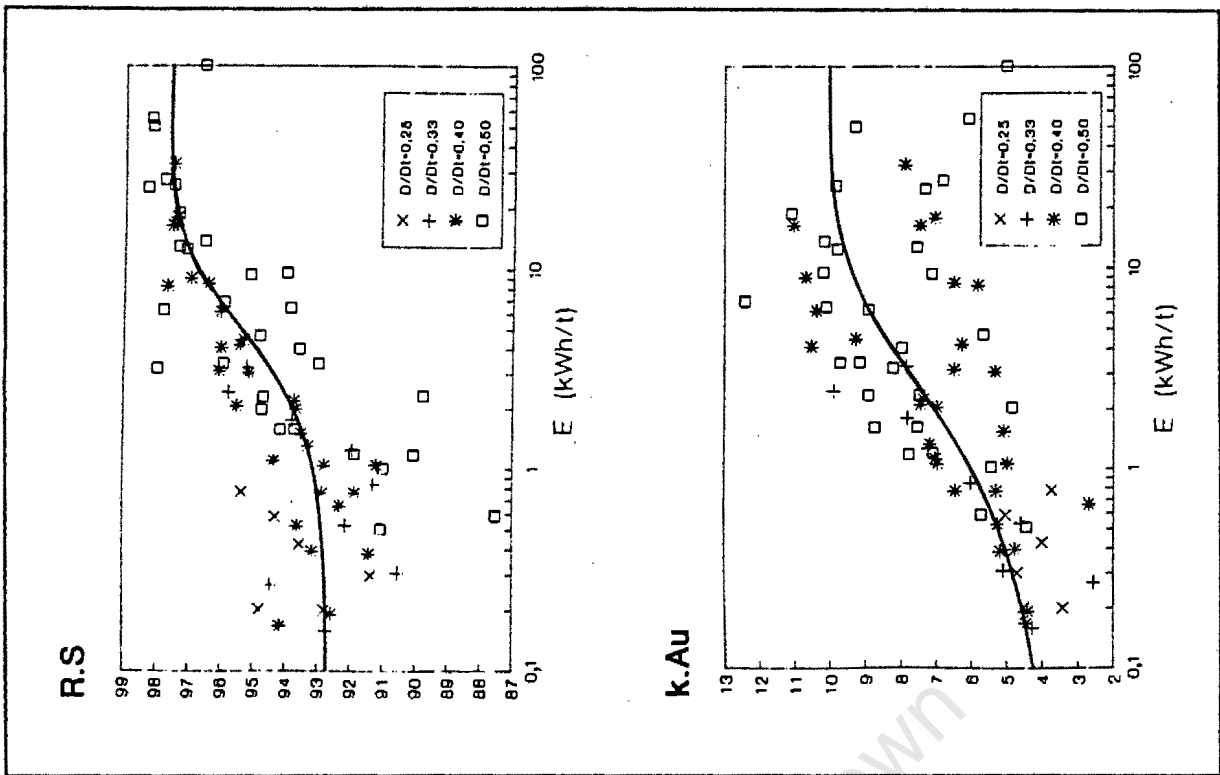


Figure 2.23 - Klimpel Parameters for Gold vs Conditioning Energy (from Stassen, 1991a)

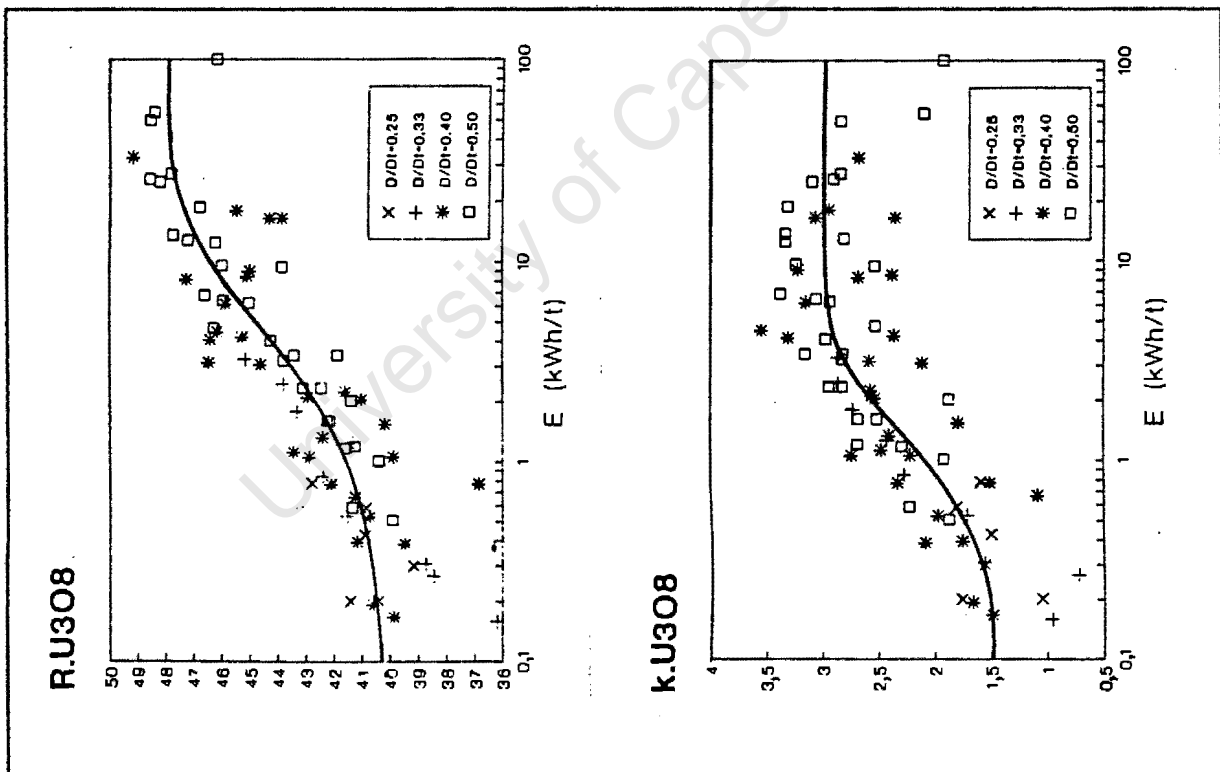


Figure 2.24 - Klimpel Parameters for Uranium vs Conditioning Energy (from Stassen, 1991a)

There are however a number of fundamental problems with this work, relating to both the experimental procedure and the analysis of the results. Chapter 3

contains a critique of the experimental procedure and a re-evaluation and re-interpretation of the data generated by Stassen.

### **2.9.2 Ralston**

Work done by Blake and Ralston [1985] and Crawford and Ralston [1988] has investigated the connection between floatability, particle size, hydrophobicity and ionic strength in the absence of other complicating influences. A technique was used in which the surfaces of quartz particles were tailored to various known surface coverages via a methylation process with trimethylchlorosilane. The technique enabled the trimethylsilyl groups to be firmly anchored to the quartz surfaces. At a fixed pH and ionic strength, the electrical double-layer properties were not found to be altered by the presence of these surface groups, neither was the van der Waals repulsion between the particles and air bubbles detectably influenced by the ultra-thin trimethylsilyl adsorption layer.

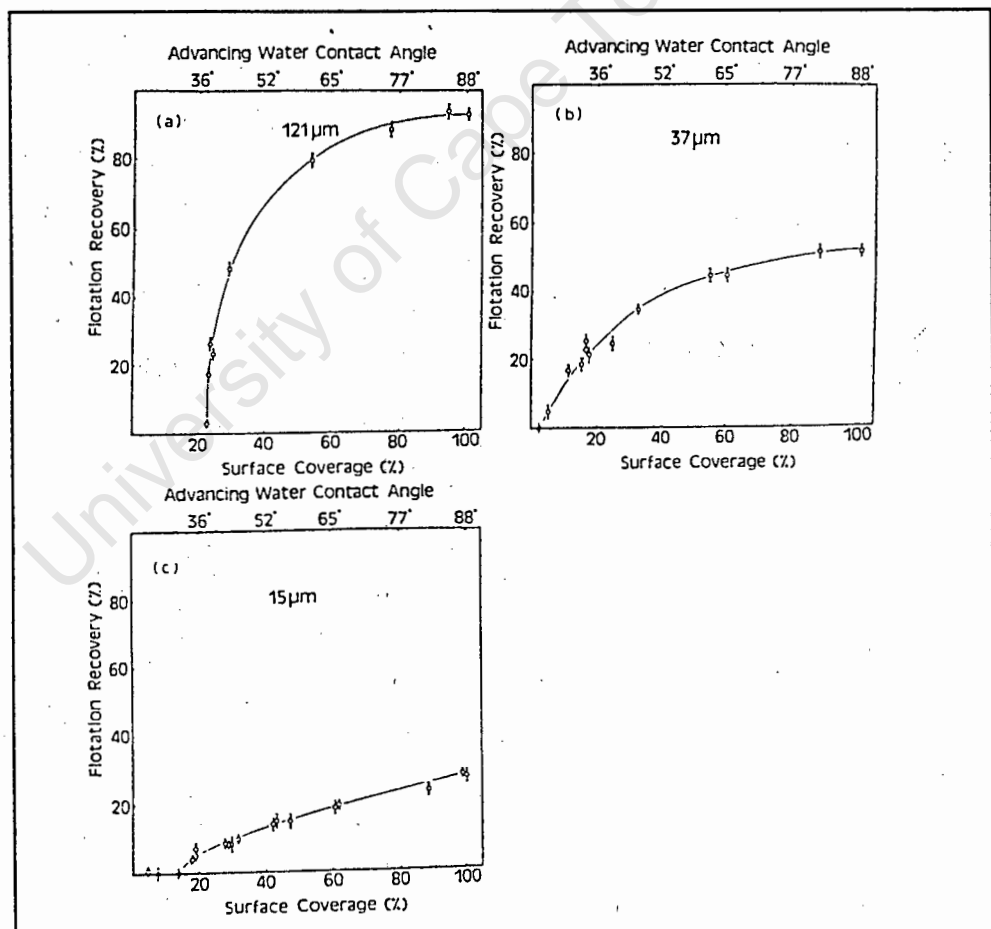
"Flotation experiments were carried out in a modified Hallimond tube; the height of the flotation column from the glass frit to the water/air interface was set at 33 cm, a figure chosen in order to reduce entrainment. High purity nitrogen was used as the flotation gas. A known mass of quartz particles, generally 1.00 g was conditioned for five minutes (method unknown - assumed to be mechanical agitation at a consistent energy input) before nitrogen was introduced. Flotation was generally carried out for five minutes."

The results obtained were analyzed under three basic headings:

#### **2.9.2.1 Flotation as a function of particle size and surface coverage**

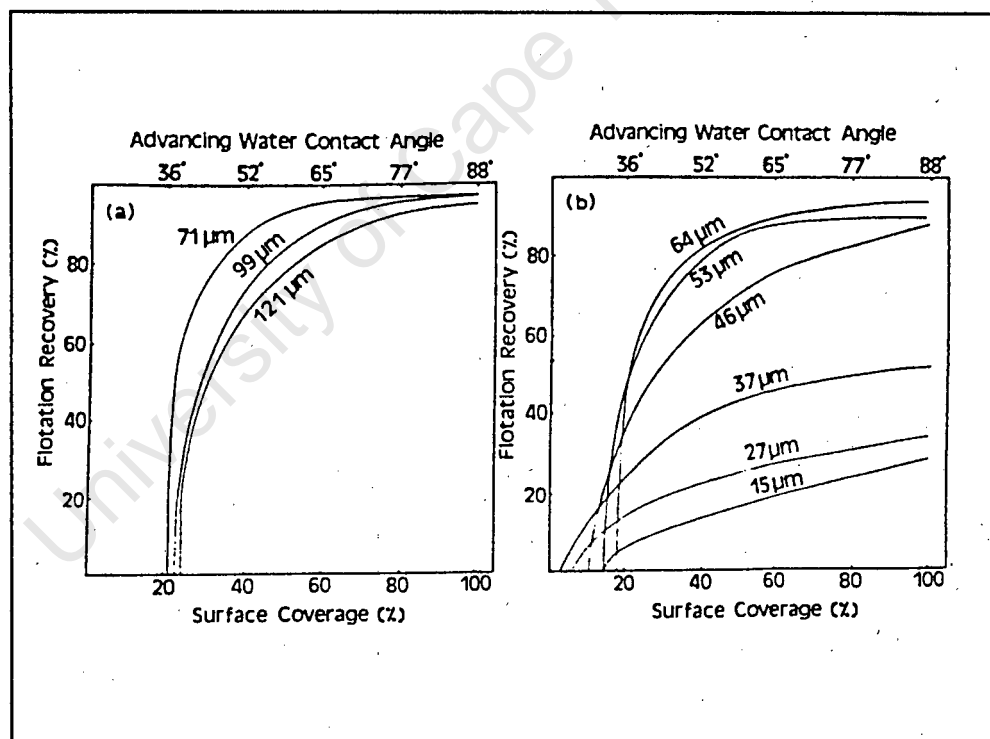
Contact angle (the primary measure of hydrophobicity) was shown to be directly related to, and easily correlated with, surface coverage of the quartz by trimethylchlorosilane. This is vital to the assumption generally made that increased surface coverage increases hydrophobicity (though this changes at very high collector dosages, when surface coverage becomes multi-layered).

Figure 2.25 shows the correlation between surface coverage (i.e. hydrophobicity) and flotation recovery for various particle sizes. Initially, at low surface coverage, no quartz floats. This corresponds to the thermodynamic situation of a positive  $\Delta G$  of attachment for mineral particles and bubble and/or large  $\tau_i$ . Then, as  $\Delta G$  becomes increasingly negative, the thermodynamic criterion is met and the reverse energy barrier becomes larger, resulting in a rapid increase in the flotation probability term  $P_s$ , as well as reduced  $\tau_i$ , increasing  $P_a$ . Hence flotation rapidly increases. Coarser particles (121 microns) show higher flotation recovery than do fine particles (15 microns). This is because coarse particles have a higher probability of attachment, associated with smaller induction time requirements, as well as higher probabilities of collision. Thus, these effects are easily explained by the kinetic and thermodynamic theory discussed in section 2.6.



**Figure 2.25 -** Effect of Surface Coverage on Flotation [Crawford and Ralston, 1988]

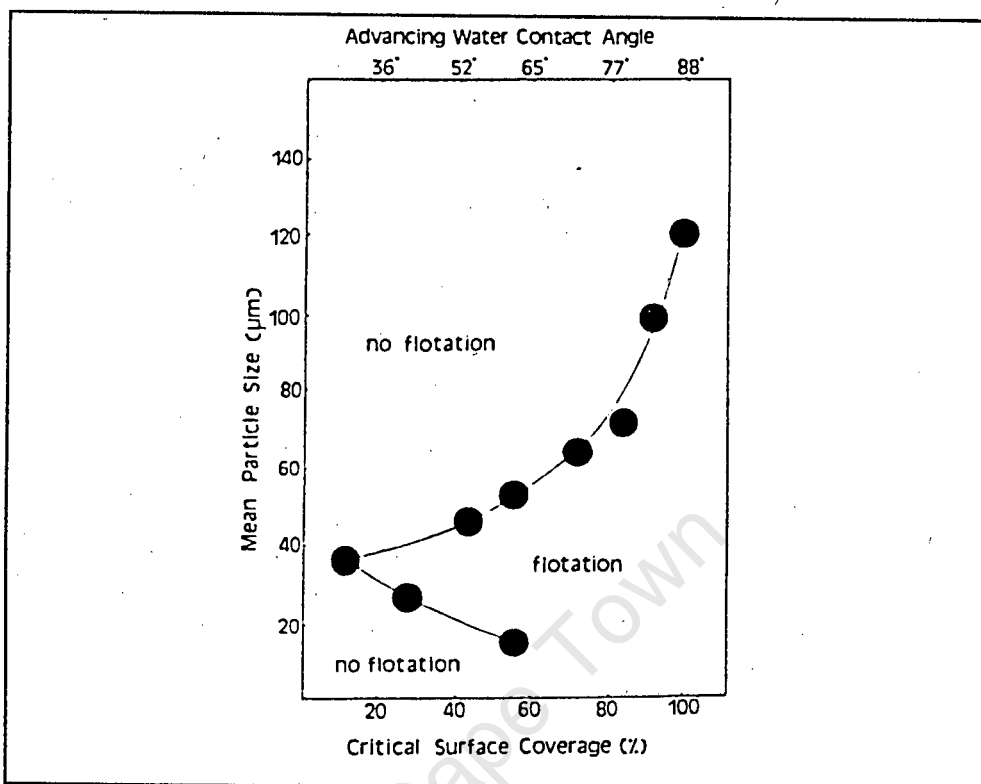
It is important to examine more carefully, at this stage, the effect of particle size on the extent of flotation, as shown in Figure 2.26. There is an optimal particle size, above and below which reduced flotation recovery is experienced. This phenomenon can be understood as the result of two different mechanisms, whose influence is maximum at opposite ends of the size spectrum. The first is the resistance to capture by bubbles: electrostatic repulsion forces keep particles and bubbles apart. This influence is measured as induction time. The magnitude of the influence of this effect is inversely related to particle size. The second mechanism is the gravitational and inertial forces experienced by the attached particle. These forces, causing fall-back, are countered by the reverse energy barrier. But the  $G_{\text{detach}}$  are surface forces. Surfaces increase more slowly than mass and thus fall-back is positively related to particle size. Hence, the flotation of large particles is limited by fall back, while small particles are less likely to attach to the bubble surface in the first place.



**Figure 2.26 -** Flotation Recovery as a Function of Surface coverage and Particle Size [Crawford and Ralston, 1988]

The critical surface coverage, below which quartz will not float regardless of flotation time, is shown in Figure 2.27. As may be seen, this is also dependent on particle size. Crawford and Ralston [1988] draw on induction time and flotation limit equations to analyze the

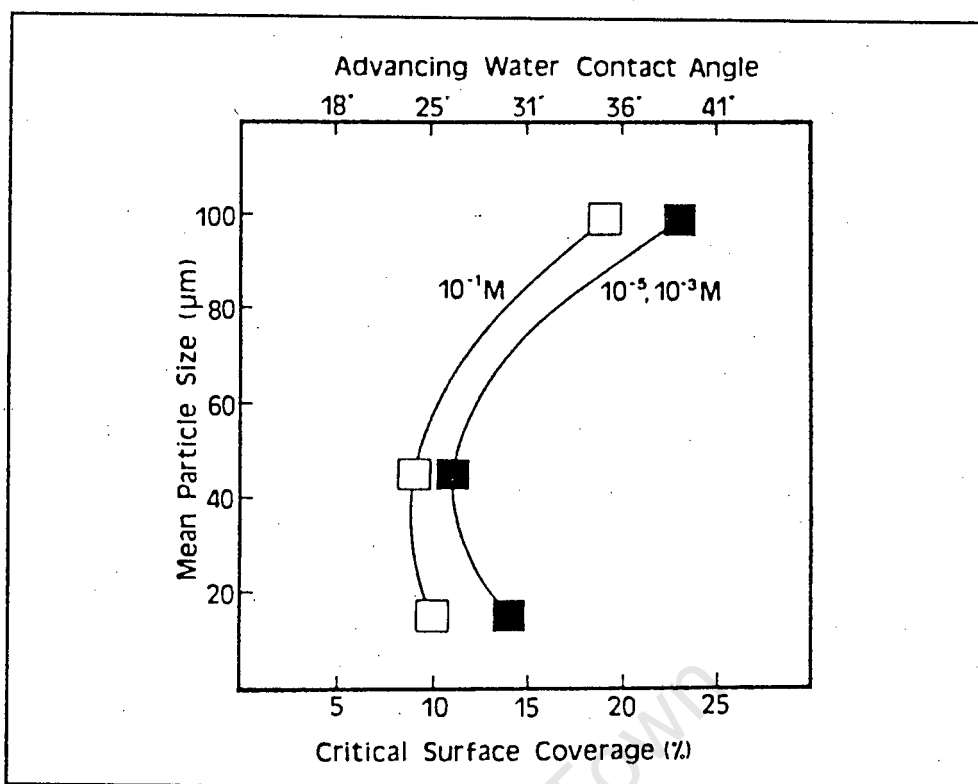
regions of floatability, but do not make any conclusions as to the reason for this phenomenon.



**Figure 2.27 -** Critical Surface Coverage for Flotation as a Function of Particle Size [Crawford and Ralston, 1988]

### 2.9.2.2 Influence of Ionic Strength on Flotation Response

Ionic strength is also seen to affect flotation, as shown in Figure 2.28 (also shown by Laskowski [1989]). Increasing the ionic strength of the pulp results in a reduction in the critical surface coverage for all particle sizes. The reason for this was discussed in section 2.6.2 in the kinetic justification of conditioning, where it was stated that induction time is an inverse function of ionic strength. The ions in solution mask the long range repulsion interactions between particle and bubble, thereby reducing repulsion and allowing more rapid approach and attachment.



**Figure 2.28 -** Effect of Ionic Strength on Flotation Recovery  
[Crawford and Ralston, 1988]

### 2.9.2.3 Flotation recovery as a function of time

Crawford and Ralston [1988] performed flotation experiments, sampling over time to gather yield data as a function of time for three different particle sizes (99, 46 and 15  $\mu m$ ). For each particle size the time dependence of flotation was also determined as a function of surface coverage. The results are shown in Figure 2.29.

The results show that coarse particles typically float very rapidly and that similar recoveries can be achieved for varying surface coverages. This finding changes as particle size decreases. For intermediate and fine particles, flotation response slows and is critically affected by surface coverage. The weak flotation response of 15  $\mu m$  particles is especially notable and correlates well with other findings where, in industrial applications, ultra-fines largely report to concentrate only because of entrainment and are not significantly concentrated.

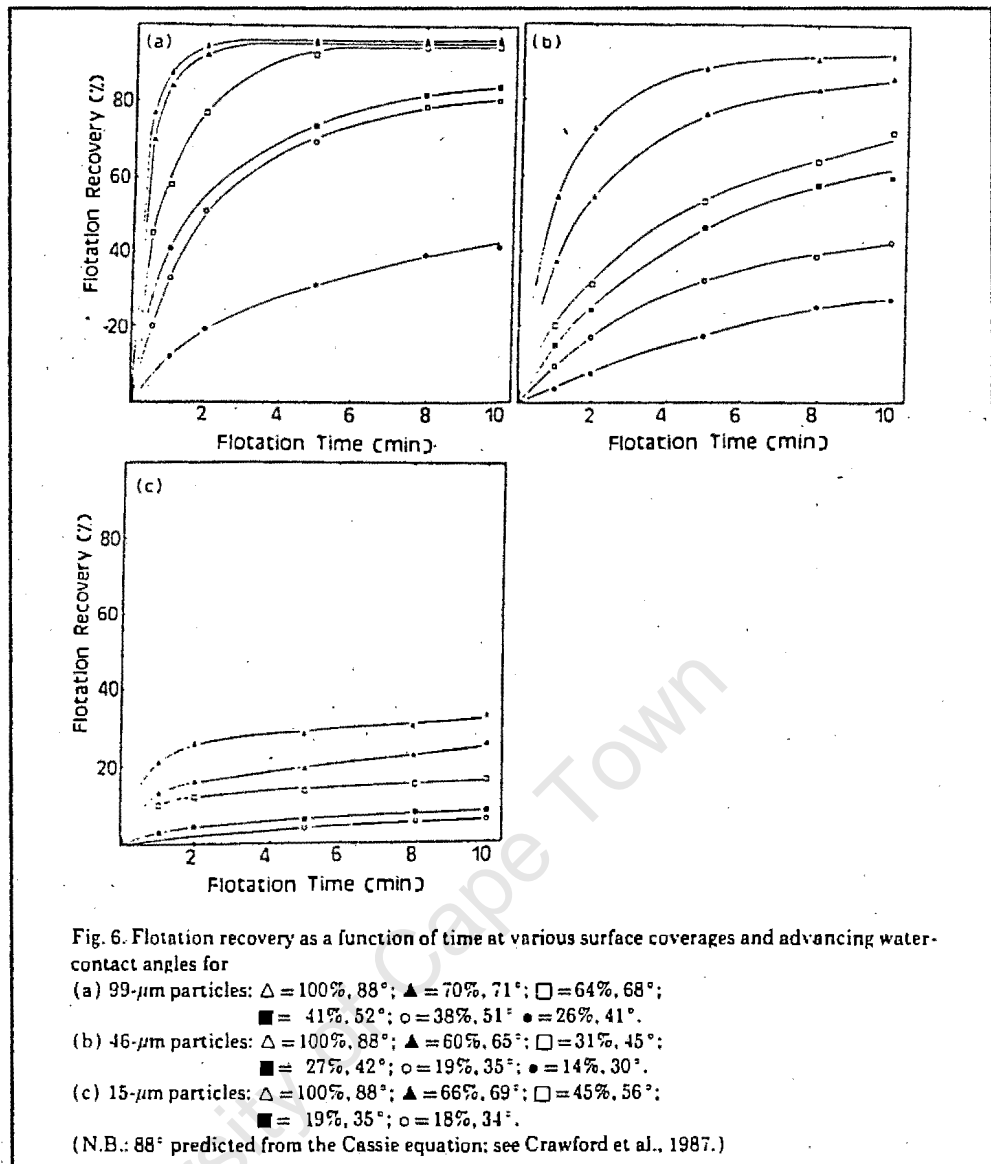


Figure 2.29 - Time Dependence of Recovery [Crawford and Ralston, 1988]

## 2.10 Summary

Conditioning is an important but variable aspect of flotation, with many systems requiring no pre-treatment before flotation while others require specialised processes. For this reason, conditioning has been largely neglected and is the least understood sub-process of flotation. It is ill-defined, with little in depth, systematic study having taken place in this field.

It was found necessary to create a definition for conditioning. Two distinct categories of conditioning were noted and defined as primary and secondary conditioning, according to their typical order of occurrence in flotation. They were defined as follows:



Primary Conditioning relates to the *physical preparation of the surface of the particles*. This includes comminution, oxidation, acid leaching and bacterial pretreatment.

Secondary Conditioning is the *process whereby prepared particles are rendered hydrophobic or hydrophilic through mixing, control of the environment and contacting with reagents*.

It was also observed that primary conditioning is very ore specific, while secondary conditioning is almost universally applied in flotation. For this reason, the work will concentrate on the most common aspect of secondary conditioning, namely the adsorption of collector onto the mineral surface in order to render it hydrophobic for flotation.

It was shown that this aspect of conditioning could be described by the theory pertaining to a heterogenous stirred tank reaction, with a surface reaction (adsorption of collector onto a mineral surface) as the primary event. This allowed the factors likely to affect the efficiency of conditioning to be determined. The variables most likely to affect conditioning efficiency were found to be (the variables to be tested in this work are indicated by italics):

ORE :	Mineral type and degree of liberation
	Grind size, affecting such features as s/v ratio
	<i>Pulp density</i>
COLLECTOR :	<i>Type, including solubility, polarity and molecule size</i>
	<i>Dosage</i>
	<i>Attachment mechanism</i>
SYSTEM :	pH
	<i>Time</i>
	<i>Mixing (power and turbulence)</i>
	<i>Method of agitation (turbulence distribution)</i>
	Temperature
	Ionic Strength

The importance of these variables of conditioning on flotation was determined by studying the factors affecting the thermodynamics and kinetics of flotation. Thermodynamically, it is necessary that conditioning make the particle to be floated hydrophobic (the explicitly stated function of secondary conditioning). All else being equal, the more hydrophobic the particle is made during conditioning, the more thermodynamically favourable the flotation. Study of the kinetic criteria for conditioning introduced the concept of induction time, which was

shown in the literature to affect the probability of attachment to rising bubbles, and hence the probability of flotation. A number of variables were shown to affect induction time, including particle size, ionic strength, the particle's charge and the slurry temperature.

Modelling of flotation was then discussed, with particular reference to the Klimpel flotation model. The uses and limitations of this model were briefly described.

Recent work in conditioning was then studied. The authors reviewed included Duchen [1980a, 1980b, 1990], Anderson [1988], Von Holt [1992], Stassen [1990, 1991a, 1991b] and Ralston [Blake and Ralston, 1985; Crawford and Ralston, 1988]. The works covered a wide range of variables of conditioning, with most of the results confirming the conditioning theory presented earlier in this chapter. The most studied variable of conditioning was energy input, with all of the research covered showing some relationship between energy input in the conditioning stage and flotation response. Stassen provided a regression function for the effect of conditioning energy input on flotation response, derived from the Klimpel flotation model. Because of the completeness of Stassen's available work and its direct relevance to this thesis, his work will be studied further in Chapter 3 to help gain a clearer insight into the conditioning sub-process and the problems associated with measurement of conditioning.

## **CHAPTER 3 - CRITIQUE OF STASSEN'S WORK**

### **3.1 Introduction**

The findings of Stassen's work have been outlined in section 2.9.1 above. His experimental results show a wide spread and a poor fit to the model he derived to predict the data points. While the data fit might be statistically acceptable owing to the large number of points, it is the opinion of the author that there are better explanations for the spread and shape of the data. In this chapter, the work of Stassen is analyzed in more detail to try to find the trends and the fundamental mechanisms causing the results.

In order to render fair criticism of Stassen's work, both the experimental method used and the mathematical model he derived need to be investigated. From an experimental point of view it is important to understand the procedure used, and to check the validity of assumptions rising out of or implicit in this. Also, the mathematical model must be thoroughly understood. In order to simplify the function, Stassen made a number of assumptions, which should be studied to check their validity. The rest of this chapter examines Stassen's experimental technique and the derivation of his function, then questions the validity of some of the assumptions made and the experimental results obtained. The data is then reviewed in the light of the analysis made.

### **3.2 Experimental Technique**

Stassen's investigation was carried out on two different samples of ore bearing pyrite,  $U_3O_8$  and gold, using n-propyl xanthate as the collector. The conditioning was performed in a large baffled tank, with the pulp being transferred to a Denver laboratory batch flotation cell for the flotation stage. The standard conditions and experimental procedure used are given below, with details taken from Stassen's thesis [1990]. All italicised text is a direct quotation from this work. Un-italicised text added by the present author is intended to aid the reader in understanding the logical progression of the discussion. Numbers in parentheses preceded by a (†) represent issues which will be discussed in detail later in the chapter.

*For the suspension of solids it is necessary to use an axial flow impeller. For the conditioning of flotation pulp two types of axial flow impeller are normally used, the pitched-blade impeller and the hydrofoil or aerofoil impeller, of which the LIGHTNIN A310 impeller is the most well-known and widely used.*

*Two ore samples (henceforward identified as ore A and ore B) were used in this investigation.*

*The following variables were selected to be studied:*

- *conditioning time*
- *impeller speed*
- *ratio of impeller diameter to tank diameter*
- *impeller type*
- *ratio of impeller height above tank bottom to impeller diameter*
- *ratio of pulp height to tank diameter*
- *type of ore*

*By different combinations of these variables it was possible to vary the conditioning energy over three orders of magnitude (0.1 to 100 kWh/t of dry ore), which is representative of conditioning energies likely to be encountered in practice.*

*The following variables were kept constant:*

- *pulp density (1300 kg/m<sup>3</sup>)*
- *conditioning and flotation temperature (25°C)*
- *pH (11,5)*
- *grind (65% -75 µm)*
- *reagent additions (100 g/t CuSO<sub>4</sub>, 60 g/t sodium n-propyl xanthate, 15 g/t Aeropromoter 3477 and 13 g/t tri-ethoxy butane)*
- *flotation cell impeller speed (1500 rpm)*
- *air feed rate*

*The experimental conditioning tank consisted of a cylindrical PVC container with a 300 mm inside diameter, flat bottom and a height of 600 mm. It had four vertical baffles of 1/12 tank diameter at 90° to one another and which*

*stretched to 10 mm from the bottom. 10 kg of dry ore, were conditioned per experiment in this container.*

*The reported conditioning times only include the times the pulp was conditioned in the conditioning tank and not the extra conditioning in the flotation cell.*

*After conditioning the contents of the conditioning tank were split on a sample splitter so that 40% was used for subsequent flotation. A laboratory size 9 litre Denver 12 flotation cell was used (†1). Approximately 13 g/t of tri-ethoxy butane was added to the conditioned pulp and conditioned for roughly 1 minute. Exactly two minutes after conditioning was completed, the air inlet was opened and flotation started. Flotation time was measured from this moment [for a total of 12 minutes]. Five concentrate samples were taken (over this period).*

*The five concentrate samples and the tails were filtered, dried, weighed, mixed and ground (to avoid fluctuation in chemical composition) and analyzed for Au,  $U_3O_8$  and S (pyrite) (†2).*

### 3.3 Derivation of Stassen's Model

The derivation of Stassen's mathematical model (taken from his Masters Thesis) is also important to the understanding of his work. Details of the derivation are given in full below. once again, italicised text is a direct quotation, un-italicised text has been added by the present author, and numbers in parentheses preceded by a (†) represent issues which will be discussed in the section below.

#### MASS TRANSFER DURING CONDITIONING

*It can be shown that the reaction between mineral particle and collector is the rate determining step during conditioning and subsequent flotation (†3). This reaction is governed by mass transfer because the diffusion of collector across a liquid film has been shown to be the rate-determining process in flotation with xanthates as collectors. The rate of mass transfer of collector A can be expressed as a first order reaction*

$$R_A = ak_L(C_A - C_A^{surf})$$

where  $R_A$  = Rate of reaction of A,  $[\text{kmol.m}^{-3}.\text{s}^{-1}]$   
 $C_A$  = Concentration of collector A,  $[\text{kmol.m}^{-3}]$   
 $C_A^{\text{surf}}$  = Concentration of collector A at the mineral surface,  $[\text{kmol.m}^{-3}]$   
 $a$  = surface area per unit volume,  $[\text{m}^2/\text{m}^3]$   
 $k_L$  = mass transfer coefficient,  $[\text{kmol.m}^{-2}.\text{s}^{-1}]$

Then

$$\begin{aligned} dC_A/dt_c &= -R_A \\ &= -ak_L(C_A - C_A^{\text{surf}}) \end{aligned}$$

where  $t_c$  = time, [seconds]

For mass transfer under turbulent conditions

$$Sh = 2.0 + cRe_p^\alpha Sc^\beta$$

with  $Re_p$  the particle Reynolds Number,  $Sh$  the Sherwood Number and  $Sc$  the Schmidt Number:

$$Re_p = uD_p \rho / \mu$$

$$Sc = \mu / \rho D_L$$

$$Sh = k_L D_p / D_L$$

At high particle Reynolds Numbers this can be approximated by

$$Sh = cRe_p^\alpha Sc^\beta$$

because the second term of this equation is much larger than the first.

Experimental data have been correlated with this equation to obtain values for (the empirical constants)  $c$ ,  $\alpha$  and  $\beta$ , eg. for spherical particles:

Generally:  $Sh = c Re_p^{3/2} Sc^{1/3}$

or:  $Sh = 1.13 Re_p^{1/2} Sc^{1/3}$

In the case of non-spherical particles even more complex equations have been derived. We continue this derivation with the general exponents for simple spherical particles (†4).

$Re_p$  can be expressed as power per unit volume as

$$Re_p = \rho^{1/3} (P/V)^{1/6} D_p^{2/3} / \mu^{1/2}$$

so that

$$Sh = k_L D_p / D_L = c [\rho^{1/3} (P/V)^{1/6} D_p^{2/3} / \mu^{1/2}]^\alpha \cdot [\mu / (\rho D_L)]^\beta$$

or

$$k_L \propto [\rho^{1/3} (P/V)^{1/6} D_p^{2/3} / \mu^{1/2}]^\alpha \cdot [\mu / (\rho D_L)]^\beta$$

If the conditions during conditioning are kept constant, then  $\mu$ ,  $\rho$  and  $Sc$  are constant so that

$$k_L \propto (P/V)_c^\gamma$$

Thus

$$dC_A / dt_c = -k_c (P/V)_c^\gamma (C_A - C_A^{surf})$$

Integration of this with initial condition  $C_A = C_A^0$  at  $t_c = 0$  and  $C_A^{surf}$  constant gives

$$(C_A - C_A^{surf}) = (C_A^0 - C_A^{surf}) e^{-k_c (P/V)_c^\gamma t_c}$$

Suppose that  $\Psi_A$  is the extent to which the surfaces of the mineral particles are coated with collector (†5).

$$\Psi_A \propto (C_A^0 - C_A) / C_A^0$$

So that

$$\begin{aligned} \Psi_A / \Psi_A^{max} &= (C_A^0 - C_A) / (C_A^0 - C_A^{surf}) \\ &= 1 - (C_A - C_A^{surf}) / (C_A^0 - C_A^{surf}) \end{aligned}$$

with  $\Psi_A^{max}$  the maximum extent to which the surfaces of mineral particles can be coated with collector i.e. at equilibrium (†6).

Normally  $C_A^{surf}$  would be very small, because the adsorption of collector is quite rapid and because the diffusion of collector across a liquid film has been shown to be the rate-determining process in flotation with xanthates as collectors.

Thus

$$\Psi_A / \Psi_A^{max} = 1 - e^{-k_c (P/V)_c^\gamma t_c}$$

If additional conditioning takes place during flotation, then

$$\psi_A / \psi_A^{\max} = 1 - e^{-k_c (P/V)_c^\gamma t_c - k_f (P/V)_f^\gamma t_f}$$

with subscripts *c* and *f* denoting conditioning and flotation respectively.

### EXPRESSION FOR *k* IN THE KLIMPEL EQUATION

It has been mentioned that floatability is proportional to the probability of flotation, i.e.

$$\Phi \propto p_c \cdot p_a \cdot p_s$$

$p_c$  the probability of collision between a mineral particle and an air bubble can be expressed as

$$p_c = (3\pi/4) \cdot D_b D_p v_{bp} N_b$$

If the conditions during flotation are kept constant, then  $p_c$  is a constant.

$p_s$  the probability of formation of a stable bond between mineral particle and air bubble can be expressed as

$$p_s = 1 - (d_v/d_v^{\text{crit}})^{1.5}, \quad d_v \leq d_v^{\text{crit}}$$

$$p_s = 1, \quad d_v \geq d_v^{\text{crit}} \quad (\text{sic: } p_s \text{ should} = 0)$$

with  $d_v^{\text{crit}}$  the maximum (critical) nominal particle diameter of a mineral particle which can form a stable bond with an air bubble.

If the conditions during flotation are kept constant,  $p_s$  is constant (†8).

For this system this means

$$\Phi \propto p_a$$

$p_a$  the probability of adhesion between mineral particle and an air bubble can be expressed as

$$p_a = \text{sech}^2 (3v_{bp}t_f/2D_b)$$

However, the concept of "induction time" introduced by this equation is not well understood and defined differently by different investigators. This has led to very large differences in the estimation of induction times. It is often defined as the difference between the instant of collision and instant of adhesion, but



there is no precise instant at which collision can be said to have occurred. This concept should only be used if more is known about induction periods.

Rather assume that  $p_a$  is proportional to the extent to which the surfaces of mineral particles are coated with collector (†7). Collector concentration through the relevant adsorption isotherm controls the surface concentration of the reagent and through this the potential adhesion capacity of the particles for the bubbles. This gives

$$p_a \propto \Psi_A$$

so that

$$\phi \propto \Psi_A^{\max} \left[ 1 - e^{-k_c(P/V)_c^\gamma t_c - k_f(P/V)_f^\gamma t_f} \right]$$

Then because  $k = N_b \phi$  the Klimpel flotation rate constant can be expressed as

$$k \propto \left[ 1 - e^{-k_c(P/V)_c^\gamma t_c - k_f(P/V)_f^\gamma t_f} \right]$$

Furthermore, if  $k \rightarrow k^{\min}$  as  $t_c \rightarrow 0$  and  $k \rightarrow k^{\max}$  as  $t_c \rightarrow \infty$ , then (†9)

$$(k^{\max} - k) / (k^{\max} - k^{\min}) = e^{-k_c(P/V)_c^\gamma t_c}$$

or

$$\ln \left[ (k^{\max} - k) / (k^{\max} - k^{\min}) \right] = -k_c(P/V)_c^\gamma t_c$$

The implicit assumption here is that conditioning in the flotation vessel is a constant and therefore is reduced out of the equation when integrated. This assumption is discussed in more detail in section 3.6.

Exactly the same form of the function can be derived for the Klimpel R parameter. The derivation for this is given in Appendix A. Thus:

#### EXPRESSION FOR BOTH KLIMPEL PARAMETERS

Summarized this means that both Klimpel parameters can be expressed as a function of the conditioning energy as

$$\ln \left[ (\phi^{\max} - \phi) / (\phi^{\max} - \phi^{\min}) \right] = -k_c (P/V)_c^\gamma t_c$$

with  $\phi$  any Klimpel parameter ( $R$  or  $k$ ); and  $\gamma$  constants which are functions only of the type of ore and type of mineral.  $k_c$  is a constant which is a function only of the conditions during flotation, the type of mineral and the type of ore.

Having progressed through the derivation of Stassen's equation, it is necessary to see how well the data may be made to fit the equation.

### 3.4 Stassen's Results and Regressed Model

Stassen used two ore types in his experimental work. A total of 74 results (data points) were obtained for ore A and 46 points for ore B. These represent different combinations of the variables listed on page 46 above. The complete results are shown in Appendix B. Below is a summary of the coefficients calculated for Stassen's derived regression model. Also included are the co-efficients of determination and statistical F values, from which Stassen inferred the applicability of his model. It was these values that Stassen used to plot the curves in Figure 2.22, Figure 2.23 and Figure 2.24 above.

Table 2 : Coefficients for Stassen's model including statistical F and  $R^2$  (Stassen, 1990)

Ore	$\phi$	$\phi^{\min}$	$\phi^{\max}$	$k_c$	$\gamma$	Coefficient of Determination $R^2$	F
Ore A	$R_{Au}$	93.8	97.5	0.0167	1.0	0.7061	173
	$k_{Au}$	3.8	10.0	0.0244	1.4	0.4556	60
	$R_{U3O8}$	40.1	47.9	0.0150	1.0	0.7646	234
	$k_{U3O8}$	1.4	3.0	0.0440	1.4	0.7068	174
	$R_S$	92.7	97.6	0.01	1.25	0.6103	113
	$k_S$	1.5	9.1	0.0161	1.1	0.8420	384
Ore B	$R_{Au}$	95.8	97.7	0.0288	1.0	0.5045	45
	$k_{Au}$	4.7	11.1	0.0229	1.4	0.6367	77
	$R_{U3O8}$	37.6	42.4	0.0172	1.05	0.7885	164
	$k_{U3O8}$	0.95	2.7	0.0273	1.4	0.5939	64
	$R_S$	95.7	97.9	0.0207	1.0	0.5888	63
	$k_S$	1.7	11.3	0.0133	1.15	0.8959	379

Stassen states:

*The statistic  $R^2$  is called the co-efficient of determination and is used to judge the adequacy of the regression model. It is a measure of the amount of*

*variability in the data explained or accounted for by the regression model. It is clear that a very high percentage (up to 89% in the case of  $k_c$  for ore B) of the variability of the data is explained by the equation (†10).*

Stassen goes on to say:

*Evaluation of the statistic  $F$  provides a second statistical test of the regression model. If  $F$  is greater than the maximum theoretical value which would be expected to occur by chance alone, it may be concluded that the distribution can not be due to chance alone. At a selected confidence level of 95% the critical  $F$ -values for the two groups A and B are  $F_{0.025,1,72}=5.26$  and  $F_{0.025,1,44}=5.39$  respectively. Because the calculated  $F$ -values are much larger than the critical  $F$ -values, it is concluded that the equation predicts the flotation behaviour of the three valuable minerals in Witwatersrand ore with respect to conditioning accurately (†11).*

### 3.5 The Model's Assumptions

Stassen's experimental technique, mathematical model and his data fit to the model have been presented. In the opinion of the author, there are several aspects which are questionable. These are discussed below, with reference to the points identified by (†#) above. A description of the expected impact of any errors introduced is also given for each point.

(†1) - It is important to note that Stassen's experiments were carried out using laboratory scale batch flotation equipment, which implies shallow unstable froth. Stassen states:

*Care was taken to ensure a constant method and rate of froth removal because of the sensitivity of flotation rate to both the rate and method of froth removal. The whole froth surface was scraped in 9 seconds and a new scraping cycle started every 10 seconds.*

However, flotation sensitivity is not limited to the method of froth removal, but is also determined by froth height and stability. This imposes additional noise and masking

of effects through fall back, which is a function of froth stability, rather than mineral attachment stability. This froth stability can actually be reduced by increased hydrophobicity of particles, and is strongly dependent on particle sizes and the mass of solids present in the froth. Stassen makes no mention of the possible error imposed by this problem.

(†2) - The next problem is in the sampling technique itself and results from the mixing of the five concentrate samples before analysing for Au,  $U_3O_8$  and S (pyrite). Stassen determined the mass yield for every interval, but only measured an average grade for all of the samples combined. Thus recovery for each of the samples is approximated as: yield times average grade. Since the Klimpel rate value ( $k$ ) is a time dependant variable, it is important that an accurate knowledge of recovery over time is gained, and not just yield. Mixing the mineral before analysis averages the mineral grades and hence requires the supposition that:

- 1) All of the mineral samples are of the same grade.

Or, failing this:

- 2) Any change in grade with time is consistent for all power inputs into the system.

While this might be a reasonable assumption for perfectly homogeneous solid particles, it cannot hold true for particles of varying size and degree of mineral liberation, as is the case here. In all cases coarser and higher grade particles will be expected to float fastest (see figure 2.31). Hence this system is immediately biased against accurate  $k$  values. Also for poorly conditioned pulp, only the purest mineral will float initially, while for well conditioned pulp a poorer grade of initial recovery would be expected. This will boost the apparent  $k$  value for well conditioned material, but will not accurately reflect the poorer grade.

Finally, mixing the samples results in the loss of useful information about the time dependency of grade for various conditioning inputs. Klimpel's work [1984] suggests that a trade-off between  $R$  and  $k$  might be expected.

(†3) - Stassen's model is derived from the assumption that adsorption of the collector onto the pyrite is diffusion controlling. This is a good assumption in as much as most studies on pyrite ores and thiol collectors indicate that diffusion is the

controlling mechanism. In Stassen's work the special case of high intensity conditioning was studied. Under these circumstances, where conditioning was very turbulent, the assumption might not be valid. The probability that diffusion may not be controlling under these conditions is discussed further in section 3.8 below. This would or could affect the interpretation of the results at the upper energy region of the test work. It is expected that as reaction rate becomes the rate controlling step, the influence of energy input into the system, and on  $k$  and  $R$  values, reduces until eventually increased intensity or duration of agitation results in no gains in flotation yield (see Figure 2.10). Thus it would be expected that Stassen's data would flatten off to constant  $k$  and  $R$  values at high conditioning energy inputs - which is indeed what happens, as may be seen in Figure 2.22, Figure 2.23 and Figure 2.24 in Chapter 2, as well as Figure 3.4 and Figure 3.5, which appear at the end of this chapter.

(†4) - Stassen chose the "general exponents for simple spherical particles" for use in the Sherwood equation. It can only be assumed that this was done for simplicity. Pyrite is a cubic crystalline structure. When the mixed mineral particles have been crushed and milled, the particles are highly irregular in shape. Moreover, only a fraction of the surface of each particle would be expected to be exposed mineral and hence an active site. Thus the particles are irregular and contain patches of active sites rather than being spherical as implied by Stassen's derivation. (It might be impossible to model this situation and hence a spherical approximation could be the most practical alternative, but this was not stated in the thesis.)

(†5) - Stassen's derivation continues by relating "collector uptake" to a "maximum extent to which surfaces of mineral particles can be coated with collector" (see equation (13) below).

$$\frac{\Psi_A}{\Psi_A^{\max}} = 1 - \frac{(C_A - C_A^{\text{surf}})}{(C_A^0 - C_A^{\text{surf}})} \quad (13)$$

$C_A =$	Concentration of collector A in solution, [kmol/m <sup>3</sup> ]
$C_A^0 =$	Concentration of collector at time $t=0$
$C_A^{\text{surf}} =$	Concentration of collector on the mineral surface

$\Psi_A =$	Extent to which surfaces of mineral particles are coated with collector
$\Psi_A^{\max} =$	Maximum extent to which surfaces of mineral particles are coated with collector

This is a non-sensical term, since thiols have been shown to accumulate on the surface of sulphide mineral to depths of as many as 80 mono-layers [Bhaskar and Forsling, 1991]. It is also a deceptive term in that it implies "surface coverage" and is indeed used by Stassen as such later in the derivation (see (†6) below). In practice the adsorption may be limited by the availability of collector in solution rather than any surface limiting or equilibrium properties, and hence "surface coverage" is not applicable for the large collector doses used by Stassen.

This is in contrast with Ralston's work [Blake and Ralston, 1985; Crawford and Ralston, 1988] where fixed surface coverages could be achieved and determined, owing to the nature of the system used. In this work, the coverage was achieved through a chemical reaction with the quartz surface, rather than adsorption.

(†6) - This concept of collector uptake is taken further and related to an "equilibrium" uptake, which as has already been mentioned is not ever reached. Collector will always be adsorbed onto the surface until exhaustion from solution [Harris and Finkelstein, 1977; Huang and Miller, 1978].

(†7) - The next stage of the model considers the classic product of probabilities discussed in section 2.6.2.

$$P_f = P_c \cdot P_a \cdot P_s \quad (3)$$

An attempt is made to relate extent of adsorption to flotation recoveries. Because of the complexity of  $P_a$  and the difficulty in defining the controlling factor, induction time, the assumption is made that  $P_a \propto \Psi_A$ , i.e. that the probability of attachment is linearly related to the extent of surface coverage of mineral with collector. There is no

scientific basis for this assumption: rather there are a number of important reasons for refuting it. These are as follows:

- 1) Pyrite is naturally floatable at around pH 4 as well as pH 11 (pH 11.5 was used by Stassen). Microflotation of pyrite at pH 4.0, carried out by the author as part of the present work, (see section 4.5.3) showed that as much as 50% of the pyrite floated without the use of any collector. Hence, while it is possible that a linear relationship exists,  $P_a$  is not directly proportional to  $\Psi_A$ .
- 2) The large xanthate collector dosage used in Stassen's experiments exceeds that necessary for maximum flotation at infinite conditioning. Thus flotation is only affected by *adsorption* up to a fraction of the maximum collector available for adsorption.
- 3) The work of Ralston [Crawford and Ralston, 1988] showed that, for quartz, the relationship between surface coverage and flotation recovery was quadratic in nature and definitely not linear (Figure 2.25). Thus for many systems,  $P_a$  is neither proportional to nor even linearly related to  $\Psi_A$ . This assumption should not have been made without substantiation.

(†8) - The above error is compounded by the assumption that  $P_s$  in the flotation probability equation is constant when physical flotation conditions are constant. This is derived from literature which states that:

$$P_s = 1 - \left( \frac{d_v}{d_v^{crit}} \right)^{1.5} \quad (14)$$

where  $d_v$  = volumetric (nominal) diameter of particle  
 $d_v^{crit}$  = volumetric (nominal) diameter of largest particle which will remain attached to the bubble

But from the kinetic and thermodynamic theory already presented in section 2.6 it is clear that collector coverage on the mineral surface will alter  $d_v^{crit}$ , because it increases the reverse reaction energy required for detachment of mineral particles from bubbles

and hence the resistance to detachment. Thus conditioning changes  $d_v^{\text{crit}}$ . Hence  $P_s$  is not a constant as stated by Stassen, but rather a function of conditioning.

(†9) - By relating rate, probability and adsorption, Stassen's model developed to look like the equation below:

$$k \propto \left[ 1 - e^{-k_c (P/V)_c^\gamma t_c - k_f (P/V)_f^\gamma t_f} \right] \quad (15)$$

where	$k$	= Klimpel rate constant
	$k_c, k_f$	= proportionality constants
	$P$	= power input
	$V$	= volume of slurry
	$\gamma$	= proportionality constant
	$t$	= time
	subscript c	= conditioning stage
	subscript f	= flotation stage

This is then integrated over time, using  $t_c = 0$  and  $t_c = \infty$  as boundary conditions to give:

$$\ln \left[ \frac{(k^{\max} - k)}{(k^{\max} - k^{\min})} \right] = -k_c (P/V)_c^\gamma t_c \quad (16)$$

It is important to note that in going from (15) to (16), the influence of conditioning in the flotation vessel falls out of the equation. Initially this might seem valid since all manipulated variables in the flotation stage remain constant. The next subsection (3.6) however shows that this is not true, with the result that the effect of conditioning during flotation cannot be removed from equation (16).

(†10) - Stassen's claim that "a very high percentage of the variability of the data explained is by the equation" is highly debatable. The median values for  $R^2$  are 0.7061 and 0.6367 for ore A and ore B respectively. This implies that a logarithmic equation



utilising 4 variables could not account for, on average, 35% of the variability of the data. This is a very poor fit for such a malleable and complex equation!

The above begs comparison with the ability of simpler equations to model this data. Linear models were generated using a statistical computer package and with no reference to any theoretical basis. The results are listed in Table 3 below. The form of the function was:  $\phi = a + b.P + c.t + d.P^2$ . It is interesting to note the similarity of the  $R^2$  results to those achieved by Stassen's equation. While Stassen's model does have consistently slightly higher  $R^2$  values, it must be noted that the time and power variables have been spaced exponentially, thus better suiting a logarithmic compression of this variable rather than linear analysis. Also, there is obviously a diminishing return on input in such a process, which would benefit an exponential function.

Table 3: Linear Residual Errors Compared with Stassen's Errors

Ore A $\phi$	Linear $R^2$	Linear F	Stassen $R^2$	Stassen F
$R_{Au}$	0.679	36	0.7061	173
$k_{Au}$	0.589	33	0.4556	60
$R_{USOS}$	0.690	40	0.7646	234
$k_{USOS}$	0.683	37	0.7068	174
$R_S$	0.610	30	0.6103	113
$k_S$	0.728	39	0.8420	384

(†11) - Stassen concludes that large F-values imply that "the equation predicts the flotation behaviour of the three valuable mineral in Witwatersrand ore with respect to conditioning accurately". It is more likely that the flexibility of the equation presented is responsible for large F-values, rather than these high values being any reflection of the fundamental correctness of Stassen's equation. This is shown both in the high F-values for the linear models presented and the fundamental errors in the derivation of Stassen's equation.

Having briefly discussed the areas of Stassen's assumptions which were felt to be problematic, it is important to analyze in more detail the expected effects of changing these assumptions. The next section covers the area of continued conditioning. This is followed by re-analysis of Stassen's data.

### 3.6 Continued Conditioning During Flotation

In Stassen's model, Klimpel rate and final recovery values are expressed in terms of conditioning power and time. The additional conditioning occurring in the flotation vessel during flotation (after the conditioning stage) is neglected; it falls out of the calculations in going from (15) to (16). However this is valid IF AND ONLY IF conditioning during flotation is constant. This appears to be true at a first analysis, but when the rates of removal are taken into consideration, it may be seen that conditioning during flotation is not constant. This may be explained as follows.

The material being floated from a cell is removed from the system at differing rates, resulting in differing amounts of conditioning in the flotation stage. To illustrate, consider two extremes of conditioning prior to the flotation stage (no prior conditioning and infinite prior conditioning). Then the results of the flotation experiments, plotted as recovery vs time, would appear as shown in Figure 3.1 below. The material which had received infinite conditioning would be removed from the slurry more rapidly than that which received no conditioning.

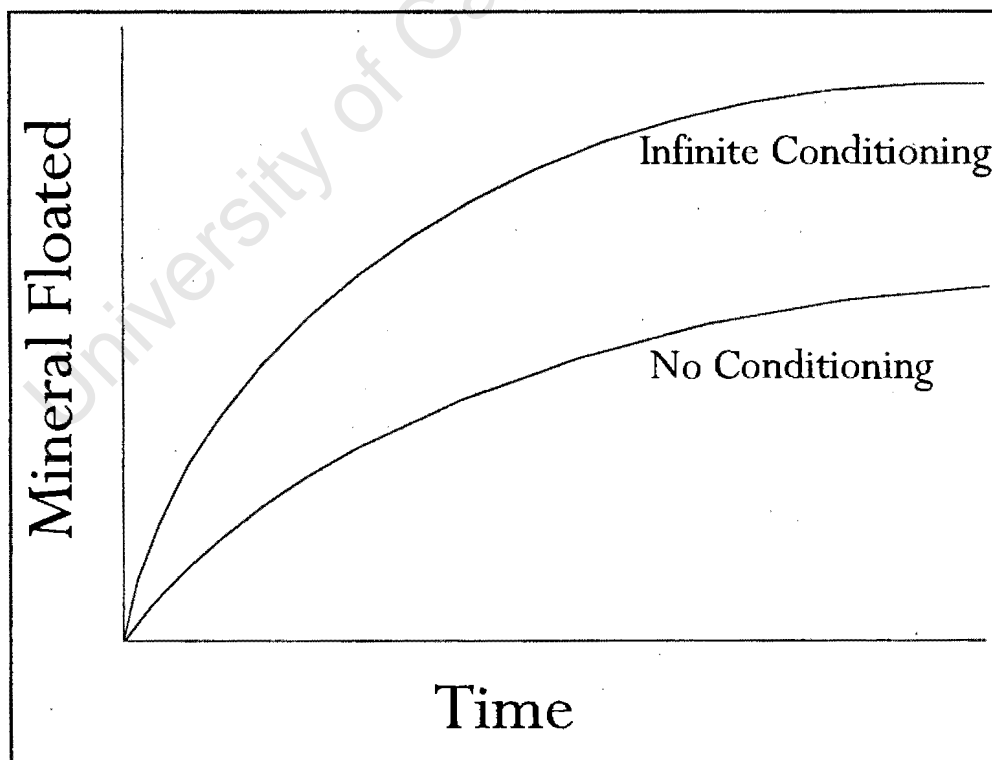
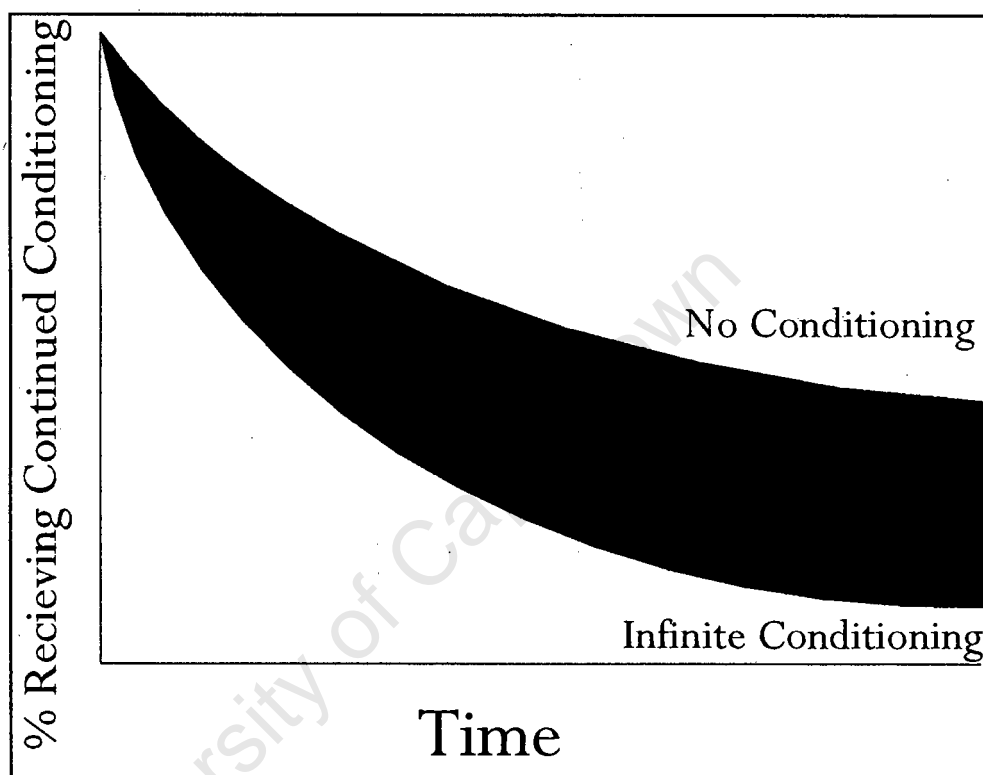


Figure 3.1 - Mineral Floated vs Flotation Time

The material which has not floated remains in the flotation vessel and receives the benefit of further conditioning. The proportion of material receiving continued conditioning for each of the cases is shown in Figure 3.2. From the Figure,

it is evident that the previously unconditioned material remains in the flotation vessel for longer than does the infinitely conditioned material - the difference corresponding to the shaded area between the two "continued conditioning" curves. Hence conditioning in the flotation cell for both cases is not the same. Material which has received some conditioning (between the two extremes of no prior conditioning and infinite prior conditioning) would lie somewhere between the two extremes in Figure 3.2.



**Figure 3.2** - % Mineral Receiving Continued Conditioning vs Time

Thus the assumption of constant continued conditioning during flotation is false. Poorly conditioned material receives the benefit of continued conditioning during flotation, while well conditioned material does not. Thus the  $k$  and  $R$  values obtained for ore which has received little prior conditioning will be artificially increased. While it can be shown that this effect is minimal for higher conditioning levels, it can be shown to be significant at low conditioning levels.

The error occurs to such an extent that continued conditioning in the flotation cell totally swamps any effect in the conditioning vessel until the energy inputs are of the same magnitudes. This may be seen by the long initial flat region in the fit to Stassen's experimental data for  $k$  values (Figure 2.22, Figure 2.23), as well as the only marginal losses in ultimate recovery ( $R$  values) predicted for even very poor conditioning

compared to very vigorous conditioning (e.g.  $R_{\min}=93\%$  and  $R_{\max}=98\%$  for pyrite). Since mineral particles have a minimum critical surface coverage requirement which must be fulfilled in order to float, and since poor conditioning is unlikely to allow this critical coverage to be exceeded, a far lower ultimate recovery would be expected at the poorer conditioning levels.

Figure 4.11 on page 107 shows much reduced recovery for reduced adsorption. This indicates that it is not that Stassen's system is poorly conditioned; rather (in the case of low energy input into the conditioning vessel) the mineral is being conditioned in the float cell instead. The Klimpel  $k$  is less affected by conditioning in the flotation cell as it is an initial term, whereas  $R$  is a cumulative term which is affected by the total energy input during the entire flotation process. This accounts for the larger predicted changes in  $k$  and very small changes in  $R$ .

The severity of this error can be checked by determining the magnitude of continued conditioning in the flotation vessel (i.e. the additional specific energy input). Oldshue [1983] states that for any particular impeller design, in an agitated vessel, a dimensionless power number can be found, which is constant for a given Reynolds number. This power number relates impeller diameter, rotational speed and power input into the system, as follows:

$$N_p = \frac{2,158 \times 10^{17} P}{N^3 D^5 \rho} \quad (17)$$

where

$N_p$	= Power number
$N$	= Rotation speed in rpm
$D$	= Impeller Diameter in mm
$P$	= Power in Watts
$\rho$	= Fluid specific gravity

Thus for a known power number, impeller diameter, pulp density and impeller speed the power input into the flotation vessel can be calculated. For this the function is rearranged to the form below:

$$P = \frac{N_p N^3 D^5 \rho}{2,158 \times 10^{17}} \quad (18)$$

Stassen supplies the following data for the flotation vessel:

$$\begin{aligned} N &= 1500 \text{ rpm} \\ \text{time} &= 1 \text{ min stirring} + 12 \text{ min float} = 13 \text{ min} \end{aligned}$$

The following necessary variables have been conservatively approximated as:

$$\begin{aligned} D &= 85 \text{ mm} \\ N_p &= 5 \text{ (lower limit for Rushton turbine)} \\ \rho &= 1.3 \text{ sg} \end{aligned}$$

Substituted into equation (18) above, this yields a total conditioning energy in the flotation vessel of:

$$P = 460 \text{ W}$$

which applied to 4 kg of ore for 13 minutes gives

$$E = 25 \text{ kWh/ton}$$

This value far exceeds most of the tested conditioning levels in the conditioning vessel, and in many cases is orders of magnitude greater. With energy inputs ranging from 0.21 kWh/t to 99.77 kWh/t in the conditioning vessel, some tests received nearly 120 times more agitation energy during the flotation stage. Fewer than 6 % of Stassen's conditioning tests received more energy in the conditioning vessel than in the flotation cell. Even if this (conservative) estimate were an order of magnitude too large, the conditioning during flotation could still be on a par with conditioning imparted in many of the tests in the conditioning vessel.<sup>3</sup>

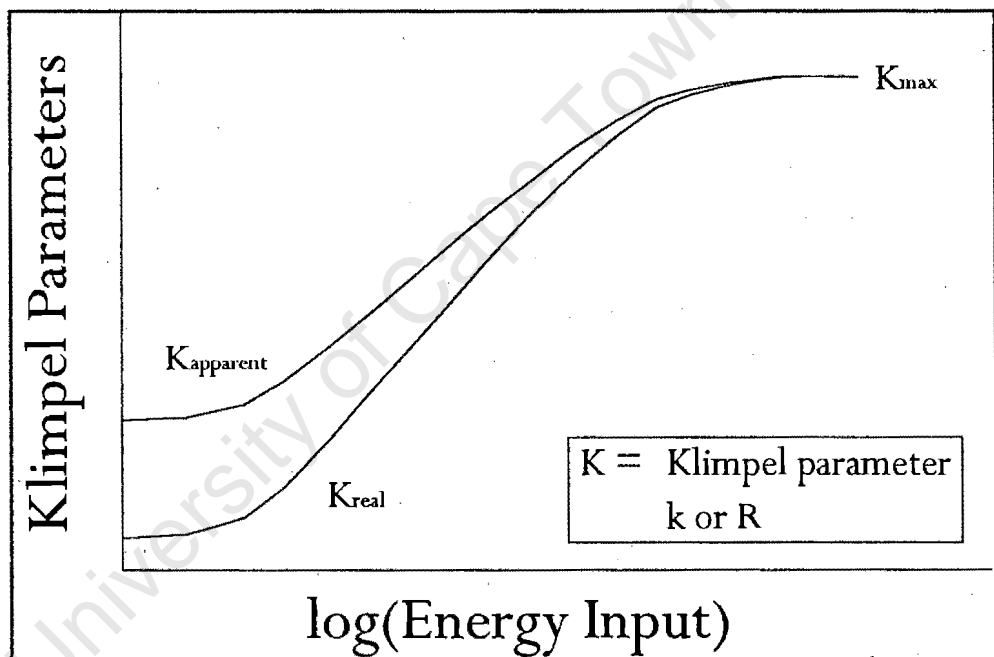
While it may be argued that much of the material will not be exposed to all of this extra energy provided during flotation, as it will have floated, this is not true for poorly conditioned material which will float slowly and hence will remain in the cell for most

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<sup>3</sup> - This is equivalent to using a 53 mm impeller, with all other variables remaining the same. If on the other hand, the impeller diameter were 100 mm then energy input during flotation would be 56 kWh/ton.

of the flotation time. The same applies to poorly floating material, which also will be exposed to the full extent of conditioning provided by the flotation stage.

As a result of this error, the measured  $k$  and  $R$  values are very different from the real  $k$  and  $R$  values. In Stassen's work  $k_{\text{apparent}} \gg k_{\text{real}}$  for poorly conditioned material and  $k_{\text{apparent}} \approx k_{\text{real}}$  for very well conditioned material. This can be represented as shown below in Figure 3.3. This error has more effect on  $R$  values, since  $k$  is determined by initial conditions (first few minutes) in the flotation vessel, while  $R$  is an equilibrium term calculated from the final flotation recoveries. The overall result is substantially higher measured Klimpel values than the real Klimpel values at low conditioning energy, with the error in measurement being reduced as the conditioning energy increases to "infinite conditioning".



**Figure 3.3** - Effect of Conditioning Energy Input on Stassen's Klimpel Parameters Showing  $K_{\text{apparent}}$  and  $K_{\text{real}}$

A partial solution, using the existing data, would be to overlay a rate function on the flotation cell's conditioning function. This would necessitate a more complex iterative solution, but would take into account decreases in flotation conditioning with increasing rates and recoveries. The greatest problem with this solution would be in determining the effects of such factors as:

- Low levels of initial conditioning, which ensure that already highly floatable particles do not adsorb unnecessary collector. These float

without much collector addition, allowing better distribution of collector to poorly floating particles.

- Removal of solids from the system, resulting in slight pulp density changes and hence conditioning power input, turbulence and collision efficiency.
- Large-scale removal of collector from solution, strongly affecting bulk concentration and hence adsorption rates.
- Large conditioning energies during flotation, totally masking effects of small initial conditioning in the conditioning vessel.
- Continued conditioning experienced during the delays between the conditioning stage and the flotation stage.
- Co-adsorption of surfactants (frothers) onto the mineral surface.
- Removal of frother over time, which will affect the efficiency of flotation of slower floating particles (or those still requiring conditioning due to low conditioning energy in the conditioning stage).
- Flotation rate (density of particles in the froth), which will influence the froth stability.

A more effective means of counteracting these problems would be to use a flotation system which to some extent eliminates the above problems. This would require the following features:

- 1) Flotation energy input should be small relative to conditioning energy input; that is:

$$(P/V)_f^y t_f \ll (P/V)_c^y t_c \quad (19)$$

This minimises the error caused by continued conditioning in the flotation cell.

- 2) The system should be frotherless and should not allow fall back of material which has left the pulp phase. This eliminates the complications caused by the froth phase, which has different criteria for optimal stability, than does the flotation phase for optimal mineral attachment to bubbles.

### 3.7 Reproducibility

Reproducibility is not discussed in Stassen's work, although experimental and sampling error is mentioned as a possible reason for the poor fit of the experimental values with the derived equation. Stassen's tests, though, did include a number of reruns of previously tested conditions.

If the errors are assumed to be normally distributed operator and sampling errors, a standard deviation may be calculated for the runs. From this data, the validity of the relationships generated for the rate and recovery may be established. This was not done by the present author, since (as has been discussed above) the data are already seriously deviant from what would be required for meaningful interpretation of the effect of conditioning energy on flotation.

### 3.8 Graphical Re-Interpretation of Data - the Importance of Power and Time vs Energy

Stassen suggested that the power and time variables in the equations for  $k$  and  $R$  can be reduced to an energy term, which implies that the results are a function of the product of time and power ( $E=P.t$ ). The following analysis from Stassen's thesis (where  $\Phi$  is either of the Klimpel parameters) implies that  $\gamma \approx 1$ :

*The closeness of  $\gamma$  to the exponent of the conditioning time (1) in the above equation (equation ) suggests that the regression model may be approximated as a function of conditioning energy,  $E \propto (P/V)^{\gamma} t_c^{\gamma}$ , giving:*

$$\ln [ (\phi^{\max} - \phi) / (\phi^{\max} - \phi^{\min}) ] = -k^* E^{\gamma}$$

Thus:

$$\Phi = \Phi^{\max} - \Delta \Phi . e^{-k_c (P/V)_c^{\gamma} t_c} \quad (20)$$

is reduced to:

$$\Phi = \Phi^{\max} - \Delta \Phi . e^{-k_c^* E^{\gamma}} \quad (21)$$



*It is clear that there is close correlation between the Klimpel parameters and the conditioning energy and that this equation may be used to predict both Klimpel parameters for all three valuable minerals accurately.*

*All the remarks just made concerning the coefficients of determination and F-values (in Table 2.) also hold for [ the new values ]. Comparison of the coefficients of determination and F-values reveals that both equations (ie. as a function of  $E'$  and  $P'$  t respectively) account for the variability in the data with the same degree of adequacy.*

Table 4 below (from Stassen's thesis) gives a comparison of the  $R^2$  and F-values for both of Stassen's regressions (ie. using P and t versus using E in the equation).

Table 4:  $R^2$  and F-values for both of Stassen's Equations

Ore	$\phi$	P and t equation $R^2$	F for P and t equation	E equation $R^2$	F for E equation
Ore A	$R_{Au}$	0.7061	173	0.7077	174
	$k_{Au}$	0.4556	60	0.4238	53
	$R_{U_3O_8}$	0.7646	234	0.7668	237
	$k_{U_3O_8}$	0.7068	174	0.6530	136
	$R_S$	0.6103	113	0.6137	114
	$k_S$	0.8420	384	0.8542	363
Ore B	$R_{Au}$	0.5045	45	0.5126	46
	$k_{Au}$	0.6367	77	0.5258	49
	$R_{U_3O_8}$	0.7885	164	0.7973	173
	$k_{U_3O_8}$	0.5939	64	0.4545	37
	$R_S$	0.5888	63	0.5979	65
	$k_S$	0.8959	379	0.8924	365

The correlations may indeed be seen to be very similar. However, while reducing power and time to an energy term may appear to be a simplification, Stassen has not really simplified or improved the equation at all. The similarity in  $R^2$  and F-values is inevitable. The equation still contains four regressed variables, and maintains the same basic logarithmic shape. It would be difficult to achieve different results using the new equation! Thus Stassen has made no progress by "simplifying" the logarithmic term to energy. What may have been of value is if  $\gamma$  could have been removed from the equation, reducing the number of regressed variables to 3.

Instead, a new term, energy, has been introduced, with wholly new implications on the conditioning process. The reader is led to a conclusion which may not be true and is certainly not substantiated. Two independent variables, power and time, have been

combined into one (energy) using  $E = P \cdot t$  and made linearly dependant in equation (21). It is then concluded that energy input into the system is the important factor affecting conditioning, rather than either power or time. But, as has been seen with the kinetics and thermodynamics of adsorption, two intimately linked variables such as these can have very different effects on the adsorption process. For example, when the reaction is rate controlling and diffusion is relatively quick, energy input into mixing will not improve adsorption, but extended durations will allow more adsorption to take place. It would appear that the only justification for replacing these two independent variables with an energy term is that this new model is no worse at predicting results.

On the other hand, there is ample evidence in Stassen's results to show that the power and time variables should be kept independent. This may be seen for example from Figure 3.4 and Figure 3.5. In these figures, Stassen's data have been plotted in the same way as in his thesis (c.f. Figure 2.22, Figure 2.23 and Figure 2.24), using the y-axis for the Klimpel  $k$  and the x-axis for the energy term, but the tests were colour coded according to the duration of conditioning. If energy were the independent variable of conditioning then it should be unimportant whether the energy is added using more power in a short time, or less power over a longer period. However, if either power or time independently dominate the equation, then for any given energy input, the Klimpel  $k$  value would be dependent on whether that energy is added quickly or slowly. This would result in the Klimpel  $k$  values for short conditioning durations being consistently higher or lower for every given energy than for long conditioning times; i.e. it would be expected that banding of conditioning times would appear in the diagram. This is exactly what happens. Thus, for example, for gold at  $E \approx 3$  kWh/ton and the given conditioning times, the following values for Klimpel  $k$  were achieved (Figure 3.5):

$t = 4.5 \text{ min}$	$k = 9.70$
$t = 9 \text{ min}$	$k = 8.22$
$t = 18 \text{ min}$	$k = 7.83$
$t = 32 \text{ min}$	$k = 6.25$
$t = 72 \text{ min}$	$k = 5.31$

Thus, analysis of the data for  $k$ , splitting data by time as well as  $E$  and  $k$ , reveals that extended time gives a lower  $k$  value for equal  $E$ . This trend continues throughout the energy range, with conditioning for a shorter time at a given energy input (i.e. more power) resulting in consistently higher  $k$  values.

That is, for  $P \cdot t = \text{constant}$ :

$$P_{\text{high}}^{\gamma} \cdot t_{\text{low}} > P_{\text{low}}^{\gamma} \cdot t_{\text{high}}$$

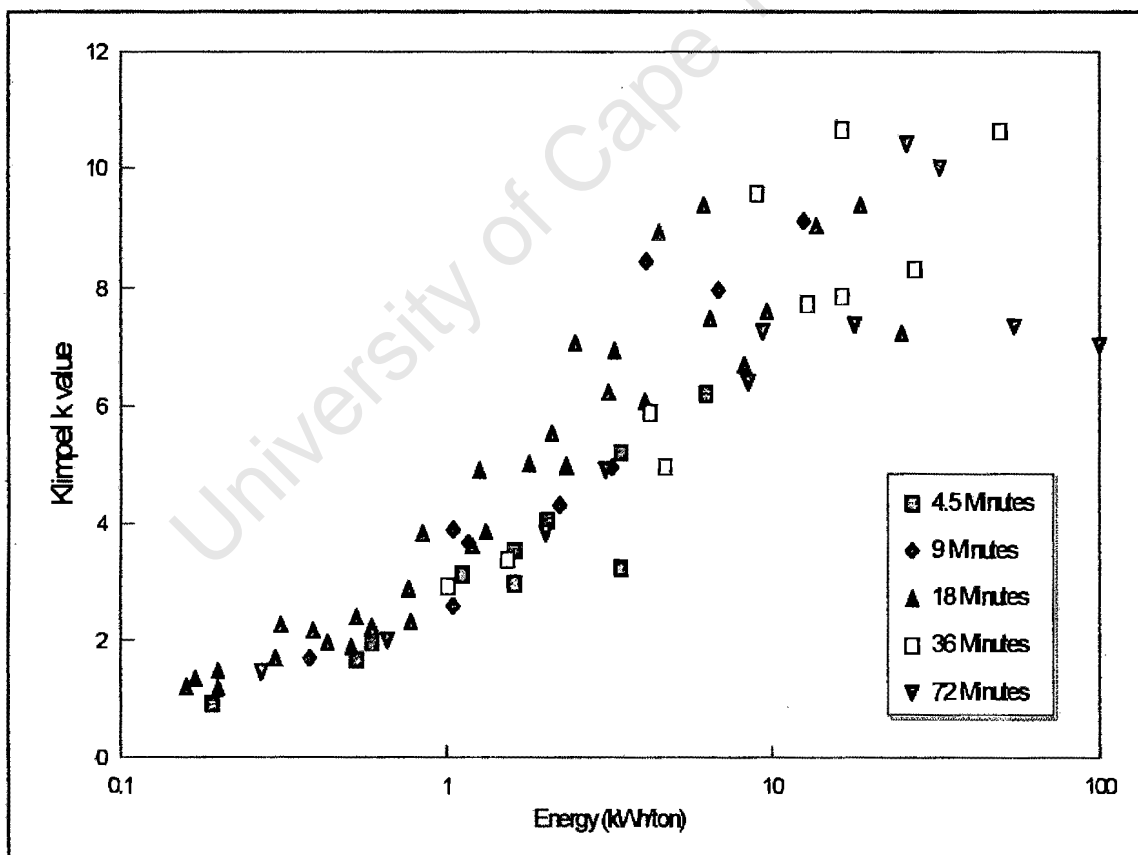
$$\text{Therefore } \gamma > 1$$

This is verified by Stassen's regressions using power and time, giving (from Stassen, 1990):

$$1.1 < \gamma_k < 1.4$$

$$1.0 < \gamma_R < 1.25$$

Thus there is both a visual and a statistical basis for maintaining both of the variables, power and time, in the equation. While reducing the terms to energy may "simplify" the equation with little increased  $R^2$  error, this would reduce the model to an empirical equation. Rather, the exact importance of power (associated with turbulence) should be investigated. This is especially important in the light of the damping effect that the large conditioning energy during flotation would have (as discussed in section 3.6).



**Figure 3.4 - Klmpel k vs Energy for Sulphur, Colour Separated wrt Time (modified from Stassen)**

Finally, another trend which is important to note is that the  $k$  values for given conditioning times appear to reach a maximum at very high energy values. This may be as a result of a

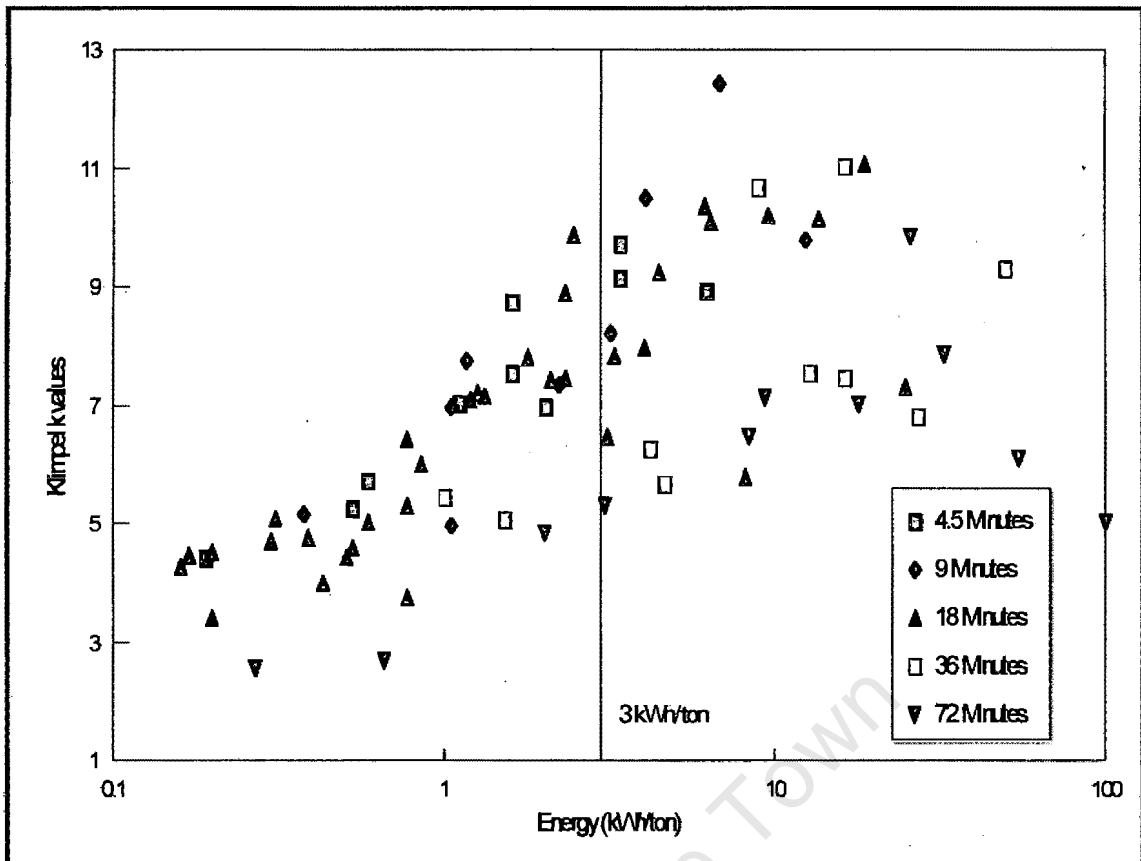


Figure 3.5 - Klimpel k vs Energy for Gold, Colour Separated wrt Time (modified from Stassen, 1990)

change in the rate controlling mechanism for conditioning. As already mentioned, at very high levels of agitation, mixing may become so efficient that diffusion is no longer the limiting stage in adsorption, rather the adsorption reaction becomes the rate controlling step. Thus additional power would not improve adsorption and hence flotation (see Figure 2.11)

### 3.9 Attrition Mechanism

The charts above (Figure 3.4, Figure 3.5) show a reduction in flotation rate at very high energy input. Stassen postulated that there was an attrition mechanism which occurred at the high energy levels, causing this drop in flotation rate. Noting the above relationship however, it is possible to refute Stassen's postulate of an attrition mechanism (for this xanthate-pyrite system). While it is probable that an attrition mechanism does exist, Stassen's data do not show it (even at very high energies, up to 99.7 kWh/t). What Stassen's data show is that to achieve such high energies, it was necessary to have a large duration of conditioning. Since time has less effect on k than does power, these extended durations have less effect on k than would large power

values. Hence the apparent drop in  $k$  with rise in  $E$  is probably a result of poor choice of axis rather than the existence of an attrition mechanism.

While this observed effect of poorer results at long conditioning times is counter to the implication from the previous section, that since additional agitation is no longer required, conditioning time would be expected to improve flotation yield, there is a possible explanation for this observation. Many xanthates have a half-life measurable in minutes or hours and this degradation could conceivably result in poorer flotation occurring when extended conditioning time is given.

### 3.10 Conclusion

While it is easy to criticise another's work, it is important to bear in mind the reason for analysing Stassen's thesis. A number of valuable lessons and useful information have been gleaned from an analysis of Stassen's results. The key elements are as follows:

Continued conditioning occurs during flotation. Because flotation is a dynamic, time dependent process, it cannot be ignored by assuming continued conditioning to be a constant. In the study of conditioning, it is necessary to minimise the power input during this stage or, better still, to eliminate it altogether.

The relationship between conditioning and flotation yield is a complex combination of thermodynamic and kinetic mechanisms. Hence, it would be better to use a simpler measure of conditioning to gain a clearer understanding of this sub-process, before attempting to relate changes in the variables of conditioning directly to flotation yield.

The froth phase complicates the conditioning versus yield relationship still further and again points to the need for another measure of conditioning.

Both power and time appear to be important variables of conditioning. Contrary to Stassen's suggestion that energy is the important factor, the effects of power and time on conditioning appear to be independent of each other. Poor mixing, as found in large vessels, would result in a diffusion controlled

adsorption process, whereas as power increases to a well mixed regime, reaction rate becomes controlling and time becomes the important variable. Stassen's data suggest that yield returns diminish exponentially with increases in energy input into the conditioning stage. There must therefore be an economic cut-off point.

Equipped with a better understanding of the conditioning process and the potential difficulties of measuring the effects of conditioning variables, it is now possible to begin designing preliminary experimental equipment and procedures for the present investigation. This preliminary work is discussed in Chapter 4 below.

# **CHAPTER 4 - DEVELOPMENT OF APPROPRIATE TECHNIQUES FOR MEASURING THE EFFECTIVENESS OF CONDITIONING**

## **4.1 Introduction**

In Chapter 2, a workable definition of conditioning was proposed, and in Chapter 3 an in-depth analysis of Stassen's previous work on conditioning was carried out. This has led to a better understanding of the conditioning process, and of the potential difficulties of measuring the effects of conditioning variables. The way is now clear to begin the design of experiments to study the effects of variables of conditioning on conditioning efficiency.

This chapter and the next cover the design stage, including the development of appropriate techniques for measuring the effectiveness of conditioning, and preliminary test results. During this stage, a number of practical problems were experienced, which both deepened understanding of the conditioning mechanisms and required minor changes in direction. These problems and their solutions have also been included in these chapters.

In order to undertake the experimental investigation, it was necessary to answer the following questions:

- 1) How will conditioning be measured?
- 3) What mineral system will be used?
- 2) What equipment and experimental technique is required?
- 4) What variables will be tested?

Once these questions were answered, and the test method was found to be effective, the work could progress to tests, results and conclusions. This chapter and the next answer each of the above questions in turn. The rest of this chapter covers the measurement of conditioning the choice of an appropriate mineral-collector system, and the

equipment and techniques to be used. Chapter 5 discusses the variables to be tested and the experimental program devised.

## 4.2 Adsorption as a Measure of Conditioning

The failure of Stassen's work to yield meaningful data demonstrated the need to divorce flotation effects from conditioning effects. By ensuring that conditioning effects are not masked by the flotation method used, more system independent observations can be made. The function of (secondary) conditioning is to render particles hydrophobic, chiefly through adsorption of collector onto the mineral surface. *Therefore adsorption is the obvious measure of conditioning effectiveness.*

Adsorption is a surface phenomenon, with collector particles arranging themselves on the mineral surface in such a way as to minimise the free energy of the system. For this reason, molar adsorption of collector will vary with both particle and collector-molecule sizes and their relative geometries. Thus molar uptake of collector onto the mineral surface (per mass of mineral) will vary according to particle grind for any given surface distribution. This surface distribution is termed "surface coverage" and is a measure of the fraction of the mineral surface covered by collector.

From Ralston's work [Blake and Ralston, 1985; Crawford and Ralston, 1988] it can be seen that "surface coverage" might be a more useful term than molar uptake, since all particle sizes coated with collector to similar surface coverages have the same surface properties, such as hydrophobicity. This is more readily understood and more system independent than molar adsorption.

The concept of surface coverage also aids with understanding the fundamental attachment mechanisms involved in adsorption, as discussed in section 4.2.1 below. The standard unit for surface coverage is a "mono-layer" of collector covering the surface. For any particle the amount of collector required for mono-layer coverage can be determined, either by using a series of experiments, described below, or through calculations based on mineral surface area and molecule size and shape.

The use of adsorption, or surface coverage, as a measure of conditioning separates the study of the effect of conditioning on flotation into two stages:



- 1) The study of the effects of conditioning on collector adsorption
- 2) The study of the effect of collector adsorption on flotation.

Thus, once the effect of conditioning on surface coverage is understood, a relationship might be developed between adsorption and floatability, much as Blake and Ralston [1985] and Crawford and Ralston [1988] were able to do with the simpler system of methylated quartz. This would achieve the results that Stassen attempted to attain. The dual model would have the additional advantage of being independent of the flotation model used. This means that the use of different flotation systems, or new developments in flotation theory, would not render the conditioning model redundant.

To develop the work to the point of predicting floatability requires not only adsorption test work, but also flotation tests. The results of these flotation tests would be used to correlate adsorption observations with flotation yields. The important features of any flotation system to be used have already been mentioned in Chapter 3: the system should have minimum turbulence and be free of frother effects.

The rest of this section discusses methods for measuring adsorption and relating adsorption to floatability, through flotation tests.

#### **4.2.1 Surface and Monolayer Coverage**

The inherent problem with the concept of surface coverage, is the assumption that mineral surfaces are homogeneous and that the collector attaches evenly on these surfaces. Studies have shown that this is not the case, since collector tends to adsorb around active sites on the mineral surface. This does not however detract from the usefulness of the concept. It is highly workable, explaining a number of important phenomena.

Surface coverage is not, in most cases, a directly measurable variable. For this reason, another variable must be used to infer surface coverage. Adsorption of collector out of solution is directly proportional to "average" surface coverage; thus the amount of collector remaining in solution can be used to infer adsorption and hence surface coverage. While this does not hold for insoluble collectors, it is true for soluble collectors such as the thiols used in sulphide flotation, or the amines used in the flotation of quartz.

As the concentration of collector on the mineral surface increases, so the packing of the collector molecules changes, as described in section 2.4 and in Figure 2.4. The observed changes correspond to specific equilibria between surface (adsorbed) and bulk collector concentrations. It is from this that mono-layer surface coverage can be calculated.

Mono-layer coverage usually corresponds to a region where adsorption remains constant despite an increase in collector addition, as described in section 2.4. Since collector removed from solution must be adsorbed, the amount of collector required to give mono-layer coverage can be measured. This is done by performing a series of tests at increasing collector dosage and plotting residual collector concentration against collector uptake. The adsorption curve flattens out at mono-layer coverage. Thereafter percent monolayer coverage can be calculated for any given removal of collector from solution, i.e:

$$\% \text{ monolayer coverage} = 100 \times (\text{Collector Uptake}) / (\text{Adsorption}_{\text{mono-layer}})$$

where  $\text{Adsorption}_{\text{mono-layer}}$  = collector uptake required for monolayer coverage

Thus, percent monolayer coverage can be found by measuring the amount of collector remaining in solution. The disadvantage of this technique is that  $\text{Adsorption}_{\text{mono-layer}}$  is specific to the size distribution and physical properties of the mineral tested. Also, it is not always possible to measure the uptake required for mono-layer adsorption, since the measurement technique may not be sufficiently sensitive to measure the plateau. It is also possible that collector will adsorb to the walls of the vessel instead of onto the mineral surface. If either of these are the case, mono-layer coverage must be approximated using knowledge of mineral and collector geometry.

In summary, a logical measure of the effect of conditioning is the extent of adsorption of collector onto the mineral surface. This is found indirectly by measuring residual collector in solution. In order to have a standard against which to measure results, mono-layer coverage is measured or calculated and collector uptake is related to this quantity.

### 4.2.2 Measuring Residual Collector in Solution

To measure residual collector in solution, the measurement technique used must be able to detect and determine quantitatively very dilute quantities of collector in the aqueous phase. The chemical complexity of the slurry in flotation does not lend itself to standard acid-base titration, especially as collectors are typically poor acids and bases dissolved in solutions of extreme pH (pH 4 or pH 11 in the case of pyrite flotation). Of the remaining techniques, UV spectrophotometry is the technique most likely to be able to isolate the collector and give accurate readings for very dilute solutions.

To be measurable using UV spectrophotometry, the collector must have an allowed UV transition, whose absorbency can be measured and the concentration equated by the Beer-Lambert law (equation (22)):

$$A = \epsilon c d \quad (22)$$

where

- $A$  = absorbency
- $\epsilon$  = extinction coefficient
- $c$  = concentration [moles/l]
- $d$  = path length [cm]

For a given known concentration of collector, the absorbency is measured and  $\epsilon \cdot d$  is calculated. The extinction coefficient,  $\epsilon$ , is constant for a given chemical, with each species having its own characteristic wavelength. Thereafter, the absorbency of a solution, measured at the collector's characteristic wavelength, need only be found to be able to back calculate the concentration of collector in solution. From this, residual collector dosage and hence collector uptake are determined.

The thiol collectors, mentioned in section 2.4, have allowed transitions, as a result of a sulphur double bond in their structure. Most amine collectors, on the other hand, do not. To measure an amine using UV spectrophotometry, it would be necessary to induce absorbency by the addition of a structure with an allowed electron transition in the UV range. Benzene type structures within a chemical have a very strong absorbency peak and are ideal for UV spectrophotometry.

### 4.2.3 Choice of an Appropriate Mineral-Collector System

The initial choice of a mineral-collector test system for the present investigation, was made on the basis of the purity of the mineral, simplicity of the adsorption mechanism and ease of measurement. The system chosen was quartz-amine. A single mineral was chosen to eliminate the complications of grade and degree of liberation. Quartz-amine flotation is also a well studied system.

However, while ideal in many aspects, the quartz-amine system proved impractical when performing adsorption tests. Thus a pyrite-thiol system was finally chosen for more detailed investigation described in Chapters 5 and 6. This is a more complex system on a micro-level than the quartz-amine system, but proved far simpler to measure. Both systems are discussed below.

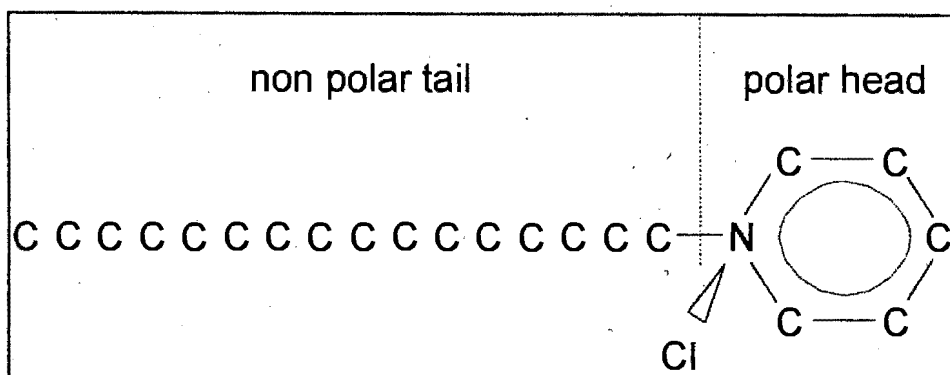
#### 4.2.3.1 Quartz-Amine System

**Quartz** is widely available in pure form and large quantities. It is naturally hydrophilic, allowing for a wide range of flotation results (0 to 100%). It has the added advantage of being a well studied mineral, where the attachment mechanisms are understood.

Typical quartz collectors are the quaternary amines. In order to measure the collector dosage by UV analysis the chosen amine should include a benzene-type ring. The available collector fitting both of these requirements is **Hexadecyl Pyridinium Chloride (HPYC)**. HPYC, shown in Figure 4.1, has a pyridine-ring, giving a high absorbency in the short UV range. To this is attached a simple saturated sixteen carbon chain, which is the collector's hydrophobic tail. The molecule is a cationic collector, with a  $\text{Cl}^- \text{N}^+$  bond off the pyridine ring resulting in an  $\text{HPYC}^+$  and free  $\text{Cl}^-$  ion in the aqueous phase.

#### 4.2.3.2 Pyrite-Thiol System

Sulphide flotation is the most common commercial flotation process. Some sulphides, pyrite among them, are naturally floatable at certain pH



**Figure 4.1** - Structure of HPYC

values. The collectors used for the flotation of sulphide minerals are typically short chain thiol collectors. These collectors are discussed briefly in section 2.4. The thiols can be measured using UV spectrophotometry.

Pyrite was chosen as the sulphide mineral to be used, since it was most readily available in a fairly pure form. So as not to have any chemicals on the mineral surface before conditioning, a gravity concentrated sample of pyrite was required. Concentrate taken from under the mill linings of a commercial gold plant was used for all of this work.

Two different thiol collectors were chosen. The first was a xanthate, potassium normal butyl xanthate (PNBX), which is very commonly used in the mining industry. The second thiol collector chosen was sodium n-propyl dithiocarbamate (diC3 DTC). These two were chosen because they display different reaction mechanisms. The dithiocarbamate is expected to be chemically more predictable in its reaction mechanism, or "better behaved", than the xanthate collector. The effect of reaction mechanism on adsorption, and hence conditioning efficiency, will be studied.

There are a number of advantages to using a pyrite-thiol system, as opposed to quartz amine systems, but the added complexity creates several disadvantages. Consequently, it is necessary to understand as clearly as possible the reaction mechanisms involved, as well as the conditions required to achieve them. The rest of this section discusses the advantages and disadvantages of the pyrite-thiol system.

**(a) Advantages of the pyrite-thiol system**

Thiols, being short chain collectors, are unlikely to undergo shear-flocculation, which for the quartz-amine system was found to alter the apparent particle sizes and hence changed the flotation properties of the particles. There is no maximum limit to the shear that can be applied to the pyrite-thiol system when studying the effects of high intensity conditioning on adsorption and flotation.

Thiols are very poor surfactants. Amines, on the other hand, are both good collectors and good frothers (surfactants): this is shown in section 4.5.2.3 to result in a dual flotation mechanism. Thus it was not possible to divorce frother and collector effects in the quartz-amine system. Thiols do not display any frothing characteristics and hence frother effects are eliminated.

A large body of previous work is available, both world-wide and at the University of Cape Town, on the mechanisms of pyrite and thiol flotation. This will help to minimise the number of tests required to find "good test parameters".

Since Stassen's work also involved pyrite flotation using a thiol collector (sodium n-propyl xanthate), this work will more closely match that of Stassen. Thus the effects of time and power on conditioning will be able to be compared with those achieved by Stassen.

Finally, since pyrite flotation is commonly used in the South African mining industry, this work may have more immediate relevance to commercial concerns, than would quartz-amine studies.

**(b) Disadvantages of the pyrite-thiol system**

Thiol collector attachment to pyrite is very complex and is not completely understood, despite in-depth studies. The reaction mechanisms vary according to pH, redox potential, collector chain length, whether or not oxygen is present and the degree of oxidation of the sulphide. In order to limit the adsorption process to one mechanism only, it is necessary to

restrict the pH of the system, as well as maintaining constant mineral surface conditions.

Pyrite oxidises very readily, resulting in an oxide surface which is very reactive and readily adsorbs collector. But since large-scale commercial flotation plants operate in oxygen limiting conditions, this adsorption is artificially high. Many sources recommend storage of pyrite under inert conditions (such as an argon environment) and to use oxygen-free flotation conditions. It was not possible, in this work, to limit the free oxygen to any great degree, nor could the surface be protected from oxidation prior to flotation. Oxidation of the mineral surface was minimised, though, by placing the mineral sample in an ultra-sound bath for a constant 10 minutes, immediately before conditioning. This would have the effect of cleaning the surface of the pyrite of its oxide coating [Harris P.J., 1993].

Chemically untreated pure pyrite is scarce. As mentioned previously, a gravity concentrate was used, but it was still necessary to limit sample sizes; typically 4 g for both adsorption and microflotation tests.

### **(c) Pyrite-thiol reaction mechanisms**

Xanthates and dithiocarbamates are complex chemicals which exhibit a number of states, as shown previously for a xanthate in Figure 2.6. The states of a dithiocarbamate are shown below in Figure 4.2. As a result of these states, xanthates and dithiocarbamates are capable of undergoing numerous different reactions in the presence of sulphide minerals. These states and their consequent reaction are determined largely by the pH of the system and the mineral type. Dithiocarbamates, for example are largely ionised to state II under strongly acidic conditions, whereas state IV exists under alkali conditions only. The states IIIa and IIIb are the intermediate products and their  $pK_a$  value typically lies between 2 and 4.

The mineral used in this work is pyrite. The region of best floatability for this mineral has historically been found to be at around pH 4 and pH 11. Work at UCT has centred around pH 4. For this reason, pH 4 was

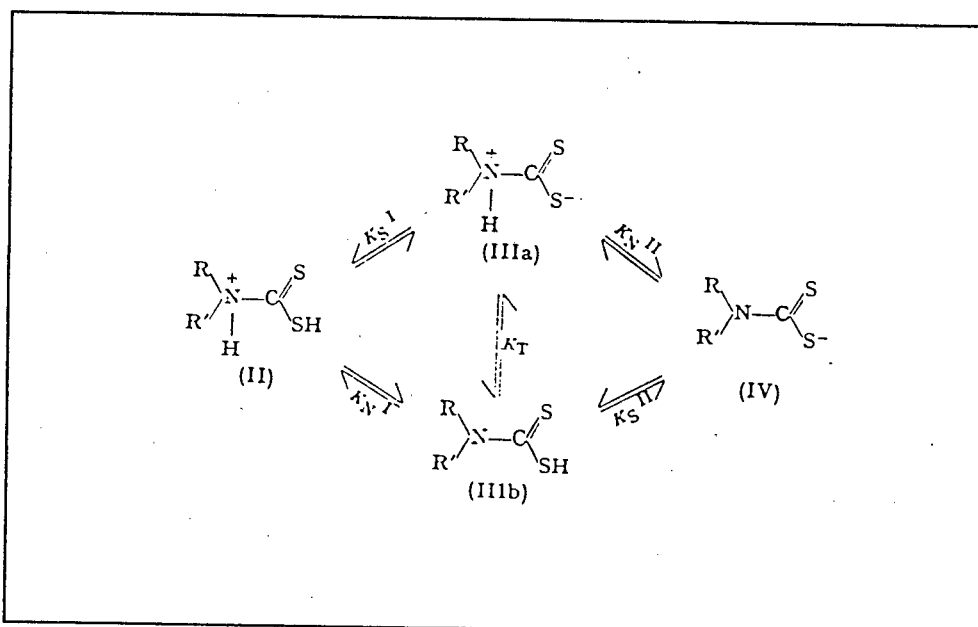
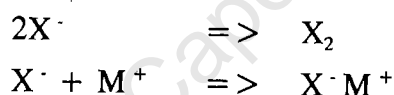
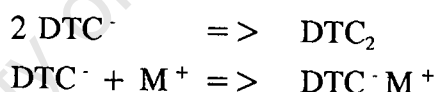


Figure 4.2 - Stable States of Dithiocarbamates

chosen as the set condition for the slurry. At pH 4 the reactions most likely to occur at the mineral surface are:



and



There are numerous other reactions that both collectors can undergo, but at this pH, the above reactions are most likely. Thus both collectors either attach to the mineral in an ionised form, or they utilise the mineral as a reaction site to form dixanthogen or  $DTC_2$ . Which of these two reaction products is formed by each collector is strongly determined by the pH and the sulphide mineral type. At pH 4 in the presence of pyrite, dixanthogen is the dominant xanthate product. Dixanthogen is insoluble in water and hence the surface reaction of  $PNBX \Rightarrow PNBX_2$  effectively precipitates PNBX out of the solution [Crozier, 1993]. Thus, provided there is pyrite present to provide the reaction site, xanthates will continue to react until the solution is totally exhausted of any xanthate. Dithiocarbamates, on the other hand, remain ionised on the pyrite surface and are hence reversibly attached to the mineral. This results in the



formation of an equilibrium between DTC's on the mineral surface and in solution [Thorn and Ludwig, 1962].

### 4.3 Relating Adsorption to Flotation: Microflotation

A flotation system which can minimise the problems inherent in the batch flotation process must be chosen to relate adsorption to floatability. The analysis of Stassen's work shows two key areas which must be addressed:

- 1) Conditioning during flotation must be much smaller than in the conditioning stage. This is so that conditioning in the flotation stage does not mask or dampen the effects of conditioning in the conditioning vessel.
- 2) The influence of the froth phase should be minimised. The froth phase is subject to different hydrodynamic criteria to those affecting the pulp phase, and thus can interfere with the flotation outcome differently, from system to system.

Two possible flotation methods are available for performing the tests:

The first possibility is column flotation. This has the advantage that there is minimum agitation in the column. Furthermore, the system can be run on a frothless basis, eliminating the complex froth phase altogether. The problem here is that a column cell is a steady-state operation, which requires complex functions to calculate particle residence time distributions. Thus, with column flotation, conditioning can only be defined in terms of a time distribution. Column flotation has a second limitation of requiring very large sample sizes, which may not be feasible when performing many tests.

The second available option is to use a batch cell that excludes the froth phase from its processes and provides a minimum of agitation. This can be achieved using a microflotation cell. Microflotation cells typically do not have a froth phase, but instead deposit the floated material in specifically designed traps. Agitation can be limited to the minimum required for particle suspension at the base of a narrow tube. Minimising the flotation time would also help to reduce conditioning error. Microflotation cells can be operated for as little as one minute to achieve useful flotation yields. The

microflotation cell has the added advantage of requiring only very small samples. Thus the features of the microflotation cell make it the flotation test equipment of choice.

## **4.4. Experimental Equipment and Procedures**

This section describes the experimental equipment used and the procedures developed for the investigation of the effect of conditioning on flotation performance. There were three aspects to the work: the conditioning experiments themselves, and the measurement of adsorption and flotation responses. These are described in the sections below, with reference to both quartz-amine and pyrite-thiol systems.

### **4.4.1. Conditioning Tests**

#### **4.4.1.1. The Conditioning Vessel**

The design of the conditioning vessel is of primary importance to this work. Good mixing within the vessel is the main requirement for conditioning. Adequate mixing is provided by a good tank design, along with correct impeller choice. For good mixing the tank should be well baffled. Too little baffling allows the liquid to swirl around with the impeller, reducing the effectiveness of the impeller. Furthermore, as particles swirl, they remain stationary relative to one another, and little mixing takes place. Too much baffling results in areas of quiescence, where particles may settle out of suspension, and again little mixing takes place.

For the impeller to be effective in suspending solids, an axial flow impeller is necessary. The down current produced by the axial force on the liquid provides sufficient turbulence to suspend the particles. Radial flow impellers, such as the traditional Rushton turbine, do not provide a vertical flow capable of maintaining particles in suspension.

Much of the conditioning work hinges on knowing the power and energy input into the conditioning vessel. It is therefore important to be able to determine the power input into the vessel. Fortunately, much work has been done by Oldshue [1983] showing that, for a given impeller type and

vessel design, the power input into the vessel can be calculated, using the concept of a power number, introduced in Chapter 3, and shown in equation (17) below:

$$N_p = \frac{2.158 \times 10^{17} P}{N^3 D^5 \rho} \quad (17)$$

- $N_p$  = Power number  
 $N$  = Rotation speed in rpm  
 $D$  = Diameter in mm  
 $P$  = Power in Watts  
 $\rho$  = Specific gravity of fluid

These power numbers have been calculated for a number of standard tank, baffle and impeller designs. Therefore, if a tank and impeller design can be found, which suit the conditioning vessel requirements, and literature values for power numbers are obtained, power input can be calculated for any given test.

#### (a) Tank Design

While there are many sources of information on tank design, they all make very similar suggestions as to the dimensions to be used. Since the information on power numbers was taken from Oldshue [1983], this reference was chosen as the main source of reference for the tank design.

For the mixing of low viscosity fluids, a vertical-cylindrical tank is recommended. This *"should be equipped with four baffles, one-twelfth of the tank diameter in width, extending vertically along the straight side of the tank and located 90° apart. Wider baffles provide slightly stronger vertical mixing currents but may act as flow dampers by reducing mass flow and reducing rotary motion."*

*"Fewer or narrower baffles allow more rotary motion or tangential mass flow, but also reduce power draw. Reducing power draw limits the energy that can be applied to the batch."* [Oldshue, 1983].

The final design of the conditioning vessel and parameters used for the test work described in this thesis is given below. The volume was chosen to minimise resource requirements, while still being sufficiently large to allow reasonable control over the manipulated variables. It was necessary to bear in mind that the contents needed to be added to the microflotation cell, without delays caused by such procedures as sample division to reduce the volume transferred. The final capacity of the cell was 400 ml.

The cell was made of PVC, and was constructed to the following dimensions:

height	= 150 mm
diameter	= 95 mm
no. of baffles	= 4
baffle width	= 9.5 mm
baffle height	= 10 cm
baffle distance from cell bottom	= 0 cm
baffle distance from cell wall	= 0 cm

#### (b) Impeller Design

As stated above, an axial flow impeller is required to keep the solid particles in suspension. The impeller chosen was a simple four blade impeller, with blades pitched at  $45^\circ$  from the vertical. This was chosen because of the ease of design and construction, as well as the simplicity with which the power consumption for this impeller can be calculated. Calculation for this design is relatively independent of size, vertical placement and depth of liquid. The impeller dimensions are shown in Figure 4.3 below.

The impeller dimensions were:

diameter	= 40 mm
blade height	= 8 mm
shaft diameter	= 5 mm

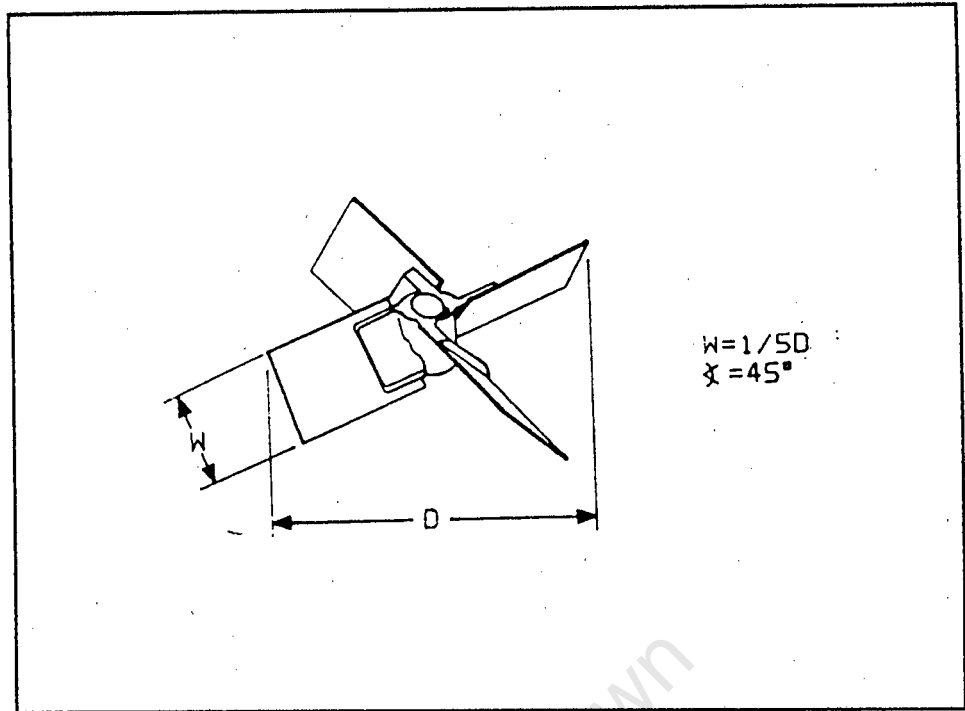


Figure 4.3 - Design of Axial Flow Impeller

#### 4.4.1.2 Power Input

The impeller was driven by a 38 W Heidolph variable-speed motor. The impeller was located 20mm (i.e. 1/2 impeller diameter) from the tank bottom. The impeller speed was measured using an electronic tachometer, with the speed set correct to an accuracy of 1 rpm.

The standard power number for this impeller in turbulent conditions (Reynolds Numbers in excess of 100) is  $N_p = 1.27$  [Oldshue, 1983]. The effect of the tank conditions, including height of impeller from base of tank and ratio of tank to impeller diameter, are calculated from charts given by Oldshue [1983]. Any deviation from the standard geometry requires a correction factor. These are determined as follows:

Standard height above tank bottom	= 1 impeller diameter
Actual height above tank bottom	= 1/2 impeller diameter
Correction factor	= 1.12
Standard baffle width	= 1/12 tank diameter
Actual baffle width	= 1/10 tank diameter
Correction factor	= 1.10

Therefore the power number for the conditioning vessel is:

$$N_p = 1.27 \times 1.12 \times 1.10 = 1.56$$

Thus, for a given impeller diameter and pulp density, any desired power input can be calculated and achieved by altering the impeller speed. This is shown in the rearrangement of equation (17) as equation (22) below:

$$N = \sqrt[3]{\frac{2,158 \times 10^{17} P}{N_p D^5 \rho}} \quad (22)$$

#### 4.4.1.3 Collector Addition Point

Dye tracer tests were performed to evaluate the best position for injection of the collector into the conditioning vessel, to maximise the rate at which good mixing was achieved. This position was found to be immediately above the impeller, approximately half the impeller radius away from the centre shaft. From visual observation of the dye, the colour was homogeneous within 3 to 5 seconds of injection when the impeller speed was 500 rpm. This indicated that mixing was rapid and delay of adsorption caused by poor mixing was negligible.

#### 4.4.1.4 Experimental Procedure

A predetermined procedure was followed strictly during the conditioning tests to try to ensure maximum reproducibility of the results. This included the method of mineral preparation, and the order and techniques used to add and mix the chemical components.

The standard procedure was developed with the subsequent analyses very much in mind, i.e. the quantification of adsorption and microflotation response. Consequently, de-ionised water was used as the base liquid in each test, to eliminate random error in the adsorption tests which might

have resulted from fluctuations in water purity. The solution chemistry was also closely controlled; for example, different pH values were maintained for the quartz-amine and pyrite-thiol systems.

The steps listed below comprise the general procedure developed for the conditioning tests; special conditions pertaining to the quartz-amine or pyrite-thiol systems are discussed in brief thereafter.

- The mineral was prepared, weighed and introduced into the conditioning vessel with the appropriate volume of liquid.
- The stirrer was switched on (at a predetermined rpm).
- The pulp was brought to the correct conditions using acid and buffer.
- Collector was injected into the pulp, near the impeller to maximise mixing speed.
- Timing began at the moment of injection of collector.

**(a) Special conditions for quartz-amine system**

The quartz used was a high purity quartz (Delmas quartz), wet sieve sized to +38-53  $\mu\text{m}$ , +75-106  $\mu\text{m}$  and +106-150  $\mu\text{m}$ . The dry ore was added to the conditioning tank, followed by the de-ionised water. The impeller was immediately turned on and the material preconditioned for one minute without reagents. This allowed time for the quartz to be completely wetted by the liquid.

The collector used was laboratory grade hexadecyl pyridinium chloride (HPYC), a 16 carbon chain alkyl pyridinium salt. Since the collector is a powder in its natural state it was first diluted to approximately 100 times the final desired concentration, which was then injected into the slurry after the one minute wetting period. Timing then began.

Amines are highly effective collectors over a large range of pH values [King, 1982], thus a neutral pH of 7 was used as the standard condition. The pH did not drift appreciably with the system used, so it was felt unnecessary to add a buffer to stabilise the pH.

### (b) Special conditions for pyrite-thiol system

As with the quartz-amine system, de-ionised water was used as the base liquid for all of the tests. A quantity of 400 ml was usually used.

The pyrite mineral used was a (Durban Roodepoort Deep) gravity concentrate, milled (laboratory scale steel rod mill) and wet sieved to +75-106  $\mu\text{m}$ . The sample, typically 4g, was cleaned of oxides using ultra-sound followed by a rinse using de-ionised water, and partially dried using a Buchner funnel to remove free water.

This cleaned pyrite was added to the de-ionised water. Stirring began, after which a buffer was added to the slurry to reduce it to pH 4. A buffer was used in preference to pure  $\text{H}_2\text{SO}_4$  to maintain the pH at a constant value, since previous work has shown [Bradshaw, 1992] that pH drift tended to occur. Changing pH would change the reaction mechanism, which might affect the results obtained. The buffer used was 0.5 ml of a standard phosphate pH 4 buffer. This was tested to confirm that it did not react with either the mineral, or the collector.

When the pH was stabilised, collector was injected into the slurry and timing began. The collectors used were laboratory grade thiols, supplied by Carbochem's research division. The xanthate used (potassium n-butyl xanthate) was mixed up from powder immediately before use, while the dithiocarbamates used, were premixed and samples were measured out using a micro-syringe. The collectors were injected into the conditioning vessel at the required point of addition.

#### 4.4.2 Adsorption Response

As discussed in section 4.2. above, adsorption was chosen as an appropriate measure of conditioning effectiveness. Thus samples were removed from the conditioning vessel at various times, and analyzed using UV spectroscopy to determine the extent of collector adsorption onto the mineral surface.



Since the technique relies on the measure of residual collector concentration in solution to determine collector uptake (see section 4.2.2.), it was important to ensure that all the collector in the samples removed from the conditioning vessel remained in solution. This meant that no mineral should be taken up with the liquid sample, as this might result in continued adsorption. This required the use of a filtering system to remove any solids taken up with the samples.

Since adsorption is a continuous process, with time being one of the important variables of conditioning, it would have been ideal to be able to sample the conditioning vessel continuously. This would have allowed an adsorption/time curve to be plotted for each test, as well as minimising the number of test runs required to determine the combined effects of other conditioning variables with respect to time. However, in practice it was not feasible to sample continuously; samples were taken on a number of occasions during a single test run.

The procedure that was finally adopted to measure the extent of adsorption that had taken place in the conditioning vessel was as follows:

- Liquid samples were removed from the vessel at given times, using a pipette.
- The liquid was immediately forced through millipore filters to remove any solids and hence "freeze" the level of collector in solution.
- The liquid was measured for UV absorbency at the characteristic frequencies for which the chosen collector displayed a peak.

The characteristic frequencies employed for each of the collectors used, and the details of the adsorption work, are given in the section on preliminary work below.

### 4.4.3 Flotation Response

#### 4.4.3.1 Microflotation cell

As discussed in section 4.3 above, microflotation was chosen as the appropriate means of determining the flotation response of samples subjected to different levels of conditioning. The microflotation cell used in the test work is based on the design of Partridge and Smith [1981] and is shown diagrammatically in Figure 4.4 below. A very low density pulp is used in the microflotation cell. The solid material is suspended using a magnetic stirrer which rests at the bottom of the cell. Stirrer speed is minimised to just suspend the mineral, thus reducing additional conditioning in the cell.

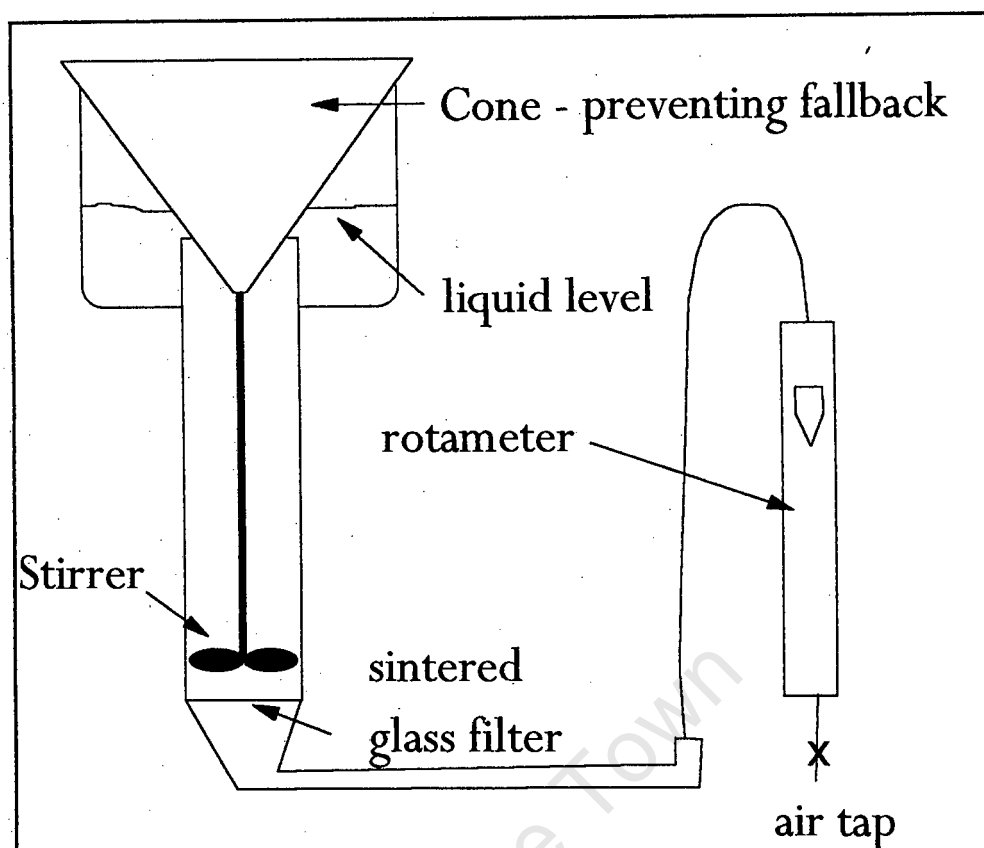
Air bubbles are created by air introduced through a sintered glass filter at the base of the cell. Bubble size increases as air rate is increased. Thus bubble size limits the extent to which air rate can be increased. The maximum air rate, which still gave acceptably small bubbles, was chosen and kept constant.

The bubbles collect hydrophobic mineral as they rise through the pulp. The long path to the top of the cell helps to minimise entrainment of gangue. Once a bubble reaches the top of the cell it is guided by the centre cone outward, where it breaks on contact with air. The floated mineral particles then drop into the collection zone at the top of the cell.

The one drawback of this technique is that only one sample can be taken per run; samples cannot be taken over a number of intervals to produce a yield vs time plot. To do this, it would be necessary to perform a number of runs at the same conditioning conditions, but different flotation times.

The dimensions of the cell are as follows:

column height	= 20 cm
column diameter	= 4 cm
cone angle	= 45°
catchment diameter	= 8 cm



**Figure 4.4 - Partidge and Smith Microflotation Cell**

Air flow rate varied, depending on the mineral used and the stirrer type employed.

#### 4.4.3.2 Experimental Procedure

The main problem with microflotation in this application is that conditioning continues after the conditioning stage. The experimental procedure must therefore minimise this by ensuring rapid transfer of the slurry from the conditioning vessel to the microflotation cell; thereafter as short a flotation test run as possible should be performed. This should include as little agitation as possible. The minimum practical duration of a flotation test run was found to be one minute. If times were reduced below this, poor reproducibility was achieved. The lack of reproducibility appears to be a result of the need for the system to stabilise, and because errors in timing were magnified by short durations.

The following procedure was devised for conducting microflotation test work (including the conditioning step):

- Dry ore was added to the conditioning vessel.
- Deionised water was added.
- The slurry is agitated for 30 seconds to wet the ore.
- Collector was injected using a syringe, while agitating.
- The material was conditioned for the required time.
- The contents of the conditioning tank were poured into the microflotation cell and additional water was used to clean all ore into the cell, as well as topping up the cell.
- Air was turned on.
- Agitation began.
- As soon as bubbles begin to rise through the glass filter timing began.
- The mineral was floated for 1 minute.
- Agitation and aeration were turned off.
- All floated mineral was collected, dried and weighed.
- Tailings were sometimes weighed to check mass balance, if necessary.

## 4.5 Preliminary Work

The following sections describe the preliminary tests carried out with the quartz-amine and pyrite-thiol systems. Adsorption and microflotation results are presented and discussed. The aim of this work was to establish "good" parameter conditions and to achieve reproducibility, so that a study of the effect of variables of conditioning on flotation could begin.

On the basis of the results obtained, it was decided to abandon the quartz-amine system and continue the investigation using the pyrite-thiol system.

### 4.5.1 Quartz-Amine Adsorption

It was first necessary to determine the absorbency peak for HPYC. From this the important wave-length to be measured could be found. The co-efficient of extinction was also calculated, to facilitate later calculations of the concentration of collector in solution from UV absorbency data. Once these were ascertained,

the suitability of residual amine absorbency testing as a measure of adsorption of collector onto the mineral could be determined.

The first conditioning tests involved the study of amine adsorption onto quartz particles closely sized to  $-75+106\ \mu\text{m}$ . Initial conditioning work was performed on a test system designed to give approximately 60% flotation of quartz after one minute using the Partridge and Smith microflotation vessel. Microflotation was not only a useful method for evaluating the floatability of the conditioned mineral: it also provided a means for determining "good" collector concentration and mixing energy. Previous work on HPYC and quartz flotation by Stonestreet [1991] provided a starting point for collector concentration and conditioning times to be used. The initial conditions, including collector dosage and conditioning times, were:

HPYC Dosage	= $0.4\ \mu\text{g}$
Conditioning time	= 2 minutes
Quartz mass	= 10 g
Liquid volume	= 200 ml
Pulp percent solids	= 5%
HPYC concentration	= $2\ \mu\text{g/l}$
Microflotation yield	= 74.4%

The conditioning procedure outlined in section 4.4.2 was followed, with the exception that only one sample was taken, at the end of the conditioning period. To ascertain the UV adsorption response of HPYC, the following tests were performed, from which important observations were made:

#### 4.5.1.1 Measurement of concentrated solutions of HPYC

High concentrations of HPYC in water give a clear peak at the allowed transition frequency of 259 nm. The coefficient of extinction was calculated as follows:

$$\epsilon = \frac{A}{c d} \quad (23)$$

where  $A = 0.225$

$$d = 1 \text{ cm}$$

$$\text{conc.} = 20 \mu\text{g/l} = 6.579 \text{ E-5 molar,}$$

$$\text{giving } \epsilon = 3420.$$

This is verified by Stonestreet's results [1991], which gave an extinction coefficient  $\epsilon = 3500$  for the absorbency peak at 259 nm.

This short wavelength requires the use of quartz cuvettes. Since amine adsorbs onto quartz, there may be some interaction between the cuvette walls and the amine in solution. This may cause loss of amine from solution and hence a lowering of the absorbency reading. Because of the small surface area of the cuvette walls, relative to the surface areas typical of finely ground quartz particles, the adsorption onto the walls was believed to be unlikely to affect the concentration readings appreciably. (This hypothesis was later tested and found to be incorrect.) Figure 4.5 shows the absorbency plot for high concentrations of pure HPYC in de-ionised water.

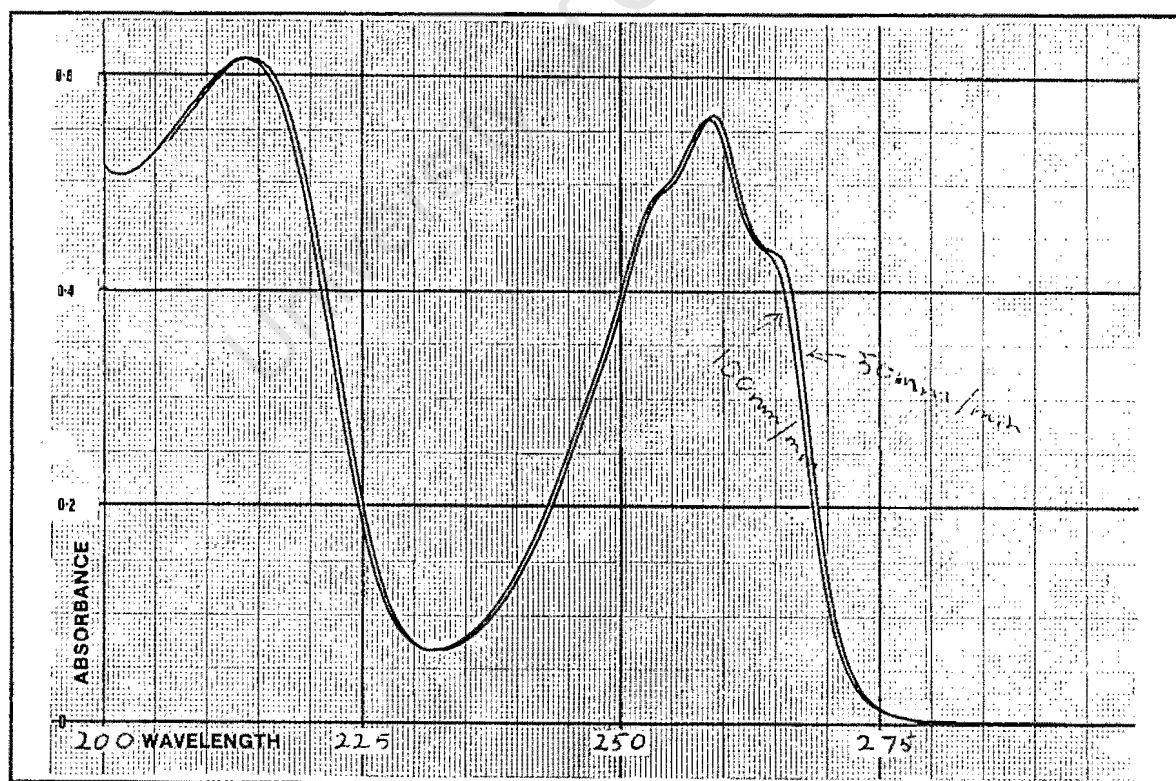


Figure 4.5 - UV Absorbency Plot for HPYC

### 4.5.1.2 Measurement of dilute solutions of HPYC

Dilute solutions of HPYC, corresponding to the concentrations of HPYC found in the conditioning vessel at the start of conditioning, gave a noisy but definite peak. The absorbency values corresponded roughly with those predicted by the Beer-Lambert law for increased dilution.

For	conc	= 2 $\mu\text{g/l}$
	predicted A	= 0.0225
	actual A	= 0.026

The readings at this dilution are at the lower limit of this technique's capacity to measure accurately. Longer cuvettes, typically 5 cm instead of 1 cm, are required to amplify the absorbency for any more dilute solutions. The minimum concentration that can be measured with any reasonable certainty is 1  $\mu\text{g/l}$  for 1 cm cuvettes and 0.2  $\mu\text{g/l}$  for 5 cm cuvettes.

In dilute solutions it was possible to test the hypothesis that the quartz cuvette had little effect on the amine in solution. A dilute sample was measured several times over a number of minutes. It was observed that, for extremely dilute solutions, the amine peak diminished over time. The drop in absorbency was very rapid initially, but stabilised quickly at a lower value than predicted by Beer's law. The loss of amine over time from dilute solutions was probably due to adsorption onto the side walls of the quartz cuvettes. While the surface area of the walls is very small, the dilution would have magnified the effect of any adsorption onto the walls. This was expected to cause measurement problems when measuring the small concentrations anticipated at the end of the conditioning process.

### 4.5.1.3 Absorbency of conditioned slurry with no collector added

A quartz slurry was conditioned without any collector added to determine the effect of impurities in the quartz on sample solution absorbency readings. A filtered liquid sample was taken from the quartz slurry after

conditioning without collector. A UV absorbency measurement of this sample gave a very high baseline when measured against de-ionised water: this was probably the result of dissolved impurities such as silicates in the slurry or ultra fine particles.

The quartz sample had been sized to +75 -106 microns by wet sieving and the liquid sample was drawn off through filter paper. The sample was well washed and filtered. Hence, the interference was more likely to be dissolved silicates than ultra-fine particles. The silicates could have dissolved off the extremely high surface area of the fine quartz particles.

The same sample procedure was used for a second test, but this time a small quantity of collector was added at the start of conditioning. After conditioning, the UV absorbency baseline was found to be lower (than it was when no collector was added), but no amine peaks could be observed. The drop in baseline indicates that there is a reaction between HPYC and the solution impurities. The lack of amine peaks after conditioning may have been the result of two possible effects: either all of the amine had been adsorbed from solution, or the silicates swamped the amine peak.

#### **4.5.1.4 Conclusions on amine absorbency spectra**

High amine collector doses were found to give strong absorbency peaks. The low doses of collector required for quartz flotation, however, approached the lower limit of the UV spectrophotometer's capacity to measure accurately.

The baseline of the liquid was shifted after quartz had been added. The probable cause of this was dissolved silicates. This shift in the base line and the extreme dilution of the collector, especially after adsorption, made UV studies impractical. While the use of a longer measurement vessel would have increased the amine peak (in accordance with Beer's law), the silicate noise would also have been amplified.



For adsorption measurement to be feasible it would have been necessary to find another system or to use another measurement technique for measuring residual collector dosages. One possibility would have been to isolate and concentrate the collector using an organic phase to absorb the collector out of the aqueous mixture. Radio-tracers could also have been used, since the sensitivity would be greatly enhanced. The simplest solution was to choose another system: the pyrite/thiol system, as described in section 4.2.3.2 above and in section 4.5.3 below.

## **4.5.2 Quartz-Amine Microflotation**

Although the quartz-amine system was eventually discarded, the microflotation tests yielded some interesting results which are worth discussing. The areas of interest include effect of collector dosage, degradation of collector, effect of conditioning time and occurrence of shear-flocculation. However, the first topic of interest is the problem of reproducibility.

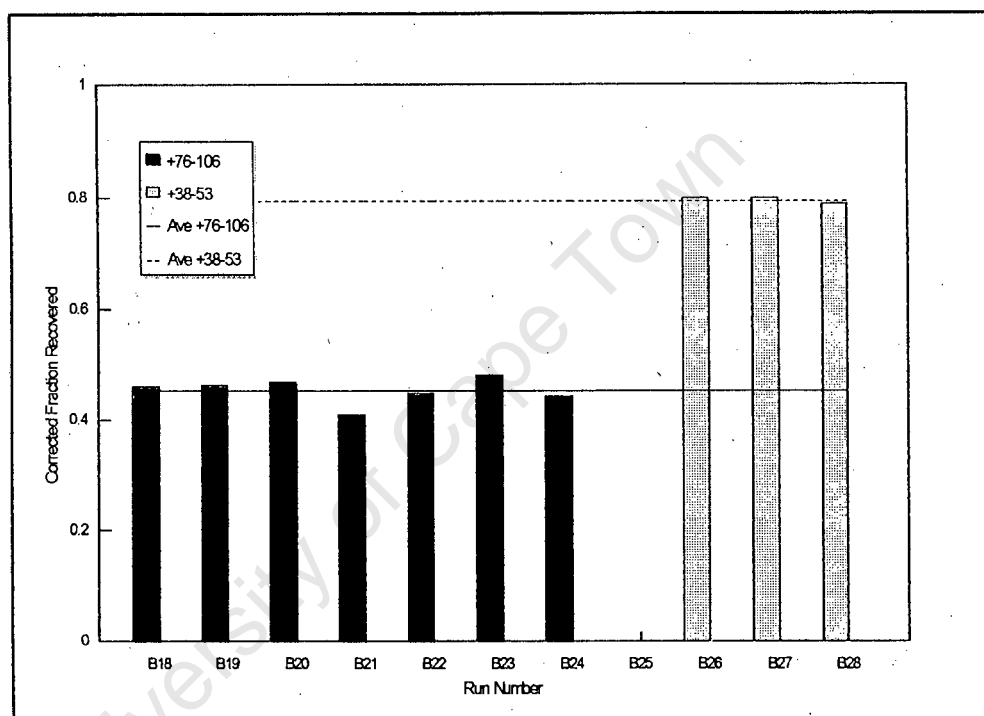
### **4.5.2.1 Reproducibility**

The small scale of microflotation makes reproducibility notoriously difficult to achieve. This system proved to be no exception. The system required gradual addition of regulatory procedures and equipment. Problem areas included:

- i) Fluctuating air flow rate - The system was very sensitive to fluctuations in air flow, resulting from a varying supply. The problem was solved by addition of an air flow rotameter, and adding a large diameter pipe between the air outlet valve and the rotameter, to absorb fluctuations in supply pressure.
- ii) Collector degradation - The collector, a dry power, was dissolved in water to a concentration of 0.1 g/l, in order to simplify the addition to the slurry. This solution was found to degrade over time, with a half-life of several days. This problem was addressed by refrigerating the solution. This completely halted the degradation process.

iii) Water quality fluctuations - random error in the microflotation results was reduced by using de-ionised water instead of Cape Town tap water in making up the slurry.

Reproducibility was eventually achieved, using quartz particles sized +76-106  $\mu\text{m}$ , and was then confirmed using particles sized +38-53  $\mu\text{m}$ . Figure 4.6 shows these results for both particle size ranges (runs B18-B28). Details of the results of the microflotation runs using quartz can be found in Appendix D.



**Figure 4.6 - Reproducibility Data Showing % Yield for Each Sample**

For quartz particles sized +76-106  $\mu\text{m}$  the standard deviation was:

$$0.021 = 2.1\% \text{ deviation on total mass}$$

For quartz particles sized +38-53  $\mu\text{m}$  the standard deviation was:

$$0.005 = 0.5\% \text{ deviation on total mass}$$

#### 4.5.2.2 Effect of collector dosage

Once reproducibility had been confirmed in the microflotation tests, a number of sets of experiments were carried out. The effect of collector dosage (into the conditioning vessel) was seen to be by far the most important variable studied. Flotation yield was directly related to

collector dosage: there was a one-to-one correspondence between dosage and yield, with flotation improving linearly with increased dosage, as shown in Figure 4.7 (runs E14, E16, E11 and E1). This can be compared to the linear region of Ralston's plot for surface coverage versus yield (Figure 2.25). It is clear therefore that for most runs, coverage was less than mono-layer. This is verified using calculations for surface area taken from collector geometry:

particle surface area	$= 2.49 \times 10^{-2} \text{ m}^2/\text{g}$
maximum collector attachment area	$= 100 \times 10^{-20}$
dosage required for mono-layer coverage	$= 1.4 \text{ ml/run}$

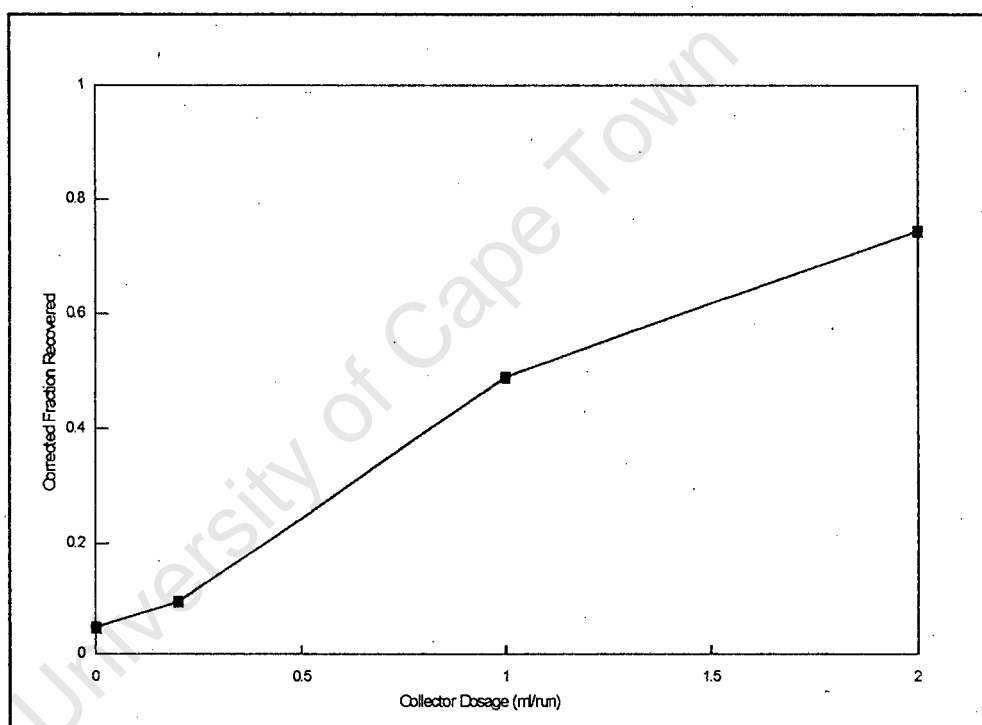
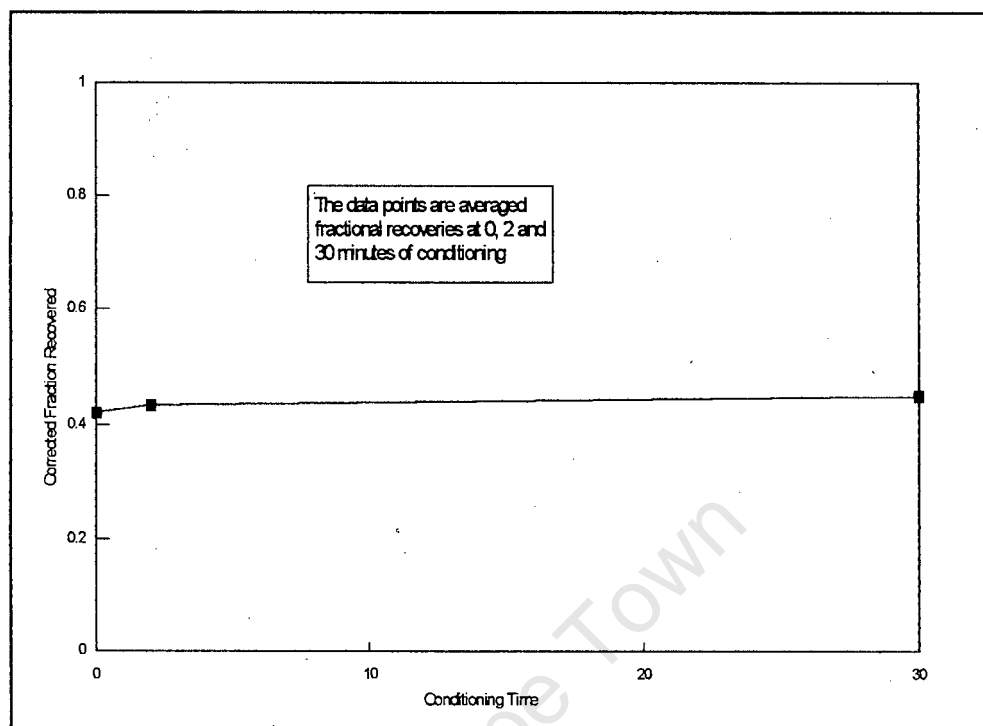


Figure 4.7 - Microflotation Yield vs Collector Dosage

#### 4.5.2.3 Effect of conditioning time

No measurable effect was seen with changing conditioning time (Figure 4.8 - runs E20, E11 and E19). This is contrary to what was expected. It is stated in the literature [Ewers, 1984; Laskowski, 1993] that amine molecules diffuse and react very rapidly and, with the small system used, it is possible that stirring within the microflotation cell during flotation was sufficient to provide complete conditioning; but other

observations indicate that another mechanism may have been responsible for this effect.



**Figure 4.8 - Microflotation Yield vs Conditioning Time**

It was noted that there were observable differences in the froth obtained with a well conditioned pulp and a poorly conditioned one. Poorly conditioned slurry gave a more stable froth, with smaller bubbles and a deeper froth. The reason for these differences is believed to be the same as the reason for there being no change in the flotation results with increasing conditioning time. The mechanism involved is postulated to be as follows: Amines are both good collectors and surfactants (frothers). Thus, collector still in solution during the microflotation step may attach to rising bubbles. On collision with mineral particles, they may then attach to the particle and serve to bond the two together. This is just as would have occurred if collector were on the mineral surface (instead of on the bubble surface). Thus different mechanisms result in similar collecting efficiencies. However, since collector (surfactant) attachment to bubbles results in increased froth stability, the froth appears visibly different.

The dual function of amines has been observed by other researchers [Wark and Sutherland, 1955; Ewers, 1984]. Also, this phenomenon of

amine on bubbles increasing flotation yield above the predicted value is described by [Digre, Sandvik, 1968]. Thus this dual mechanism both explains the observations made and is scientifically supported by previous research. It is very likely that this is why no observable improvements in flotation took place as a result of longer conditioning. *This work shows that it is important to ensure that any other collector chosen for conditioning test work is not a surfactant.*

#### 4.5.2.4 Shear-flocculation

The effect of power input on the flotation of quartz was found to be somewhat more dramatic. Since HPYC is a long chain collector, shear flocculation can play a major role under conditions of high intensity agitation. It was found that at impeller speeds of 1000 rpm and above, shear flocculation was very noticeable in the conditioning vessel (runs C4, C5 and C6). While this work does not aim to study shear-flocculation (and hence was not studied in depth), the following observations were noted:

- A critical impeller speed was required, below which no duration of agitation could induce shear-flocculation.
- Above the critical speed, longer conditioning times resulted in the formation of larger flocculated particles.
- Greater impeller speeds resulted in more rapid formation of flocculated particles.
- Flocculated particles were sufficiently stable to remain intact during flotation and filtering, but broke down on drying.
- Flotation appeared to improve with flocculation. This is believed to be a function of floatability of particle sizes and should hold especially true for very fine particles, which (un-flocculated) are poorly floating.

#### 4.5.3 Pyrite-Thiol Microflotation

The primary aim of the pyrite microflotation tests was to find the correct collector dosage range for "good" flotation. The best collector dosage to use

as a mid-point value would be the smallest dosage that provided maximum flotation yield at "infinite" conditioning. This because the same dosage at lower conditioning energies would provide a spectrum of yields, according to the extent of adsorption on the mineral surface. Larger doses would be expected to reach maximum flotation at shorter conditioning times, while smaller doses would never achieve maximum flotation. This is the area that is of interest commercially, where there is a trade-off between reagent costs and equipment or energy costs. Only diC3 DTC was used in the microflotation tests since previous work has shown that equivalent molar doses of PNBX result in comparable flotation responses to those of diC3 DTC, especially when comparing the doses required to achieve maximum flotation [Bradshaw, 1994].

Since pyrite is naturally floating at pH 4, it was important to find the extent of natural floatability of the pyrite sample (using no collector). A pyrite sample was conditioned exactly as the other samples were, in order to subject the mineral surface to the same shear and oxidation forces, but with no collector added (run no. F2 in Appendix E). It was found that 25 minutes of conditioning at 500 rpm corresponded to "infinite" conditioning, beyond which no improvement in floatability was achieved at any collector dosage. The following conditions were used:

impeller speed	= 500 rpm
buffer addition	= 0.5 ml
liquid volume	= 400 ml
pyrite mass	= 4 g
collector dosage	= 0
conditioning time	= 25 min

The pyrite yield for this run = 46.8%

Thus the minimum expected yield for any run was 46.8%. It was expected that collector adsorption would increase this to a maximum near 100%. Stassen's [1990] maximum yield was 98.6%.

Reproducibility tests for the system using no collector gave the following results (runs F2, F3 and F7):

Number of tests	= 3
Std deviation	= 0.020 = 2%

Thus the microflotation technique was felt to produce reproducible results.

The initial assumption made was that flotation would be optimum at doses which would provide mono-layer coverage. Thus the amount of collector required for mono-layer coverage was calculated, using particle surface area and collector attachment area approximations. Pyrite is a cubic crystalline structure, but surface irregularities and grinding may change the surface area. Thus a number of calculations were used to approximate surface area. The pyrite was sized to +53-75  $\mu\text{m}$  using wet sieving. It is appropriate then to assume a geometric mean size for the particles, which is 63  $\mu\text{m}$ .

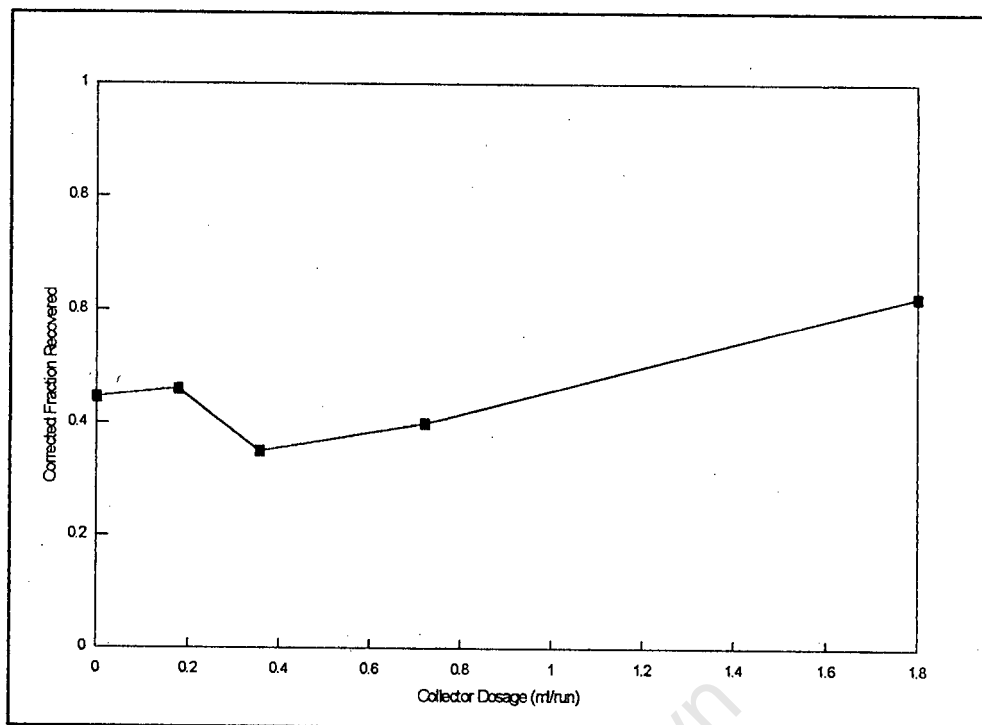
$$\begin{aligned}\text{Spherical Particle Surface Area} &= 0.01835 \text{ m}^2/\text{g} \\ \text{Minimum Cubic Particle Surface Area} &= 0.01835 \text{ m}^2/\text{g} \\ \text{Maximum Cubic Particle Surface Area} &= 0.02595 \text{ m}^2/\text{g}\end{aligned}$$

The attachment area of Sodium dipropyl dithiocarbamate  $\approx 37 \times 10^{-20} \text{ m}^2$  [Bhaskar and Forsling, 1991]. Also, the collector concentrate used contains an active ingredient of 35%, giving a concentration of  $6.94 \times 10^{-4} \text{ mole/ml}$  solution. Thus, assuming total coverage, the dosage of collector required to exactly cover the mineral surface is:

$$\begin{aligned}\text{Spherical particles} &= 8.235 \times 10^{-8} \text{ moles/g} = 0.118 \mu\text{l/g} \\ \text{Minimum cubic} &= 8.235 \times 10^{-8} \text{ moles/g} = 0.118 \mu\text{l/g} \\ \text{Maximum cubic} &= 11.65 \times 10^{-8} \text{ moles/g} = 0.167 \mu\text{l/g}\end{aligned}$$

In reality the collector adsorbs in patches of active sites and mono-layer coverage would be substantially below the above value, but it does provide a starting point for microflotation test work. Figure 4.9 (showing runs F2, F6, F4, F5 and F9) shows the flotation response for a number of collector doses of the magnitude of mono-layer coverage (results are expressed as  $\mu\text{l/g}$  of pyrite rather than as reported in Appendix E as  $\mu\text{l/run}$  of 4g of pyrite ).

These results show no improvement in flotation yield over the results achieved with no collector. This result was unexpected. It indicated that the dosage was

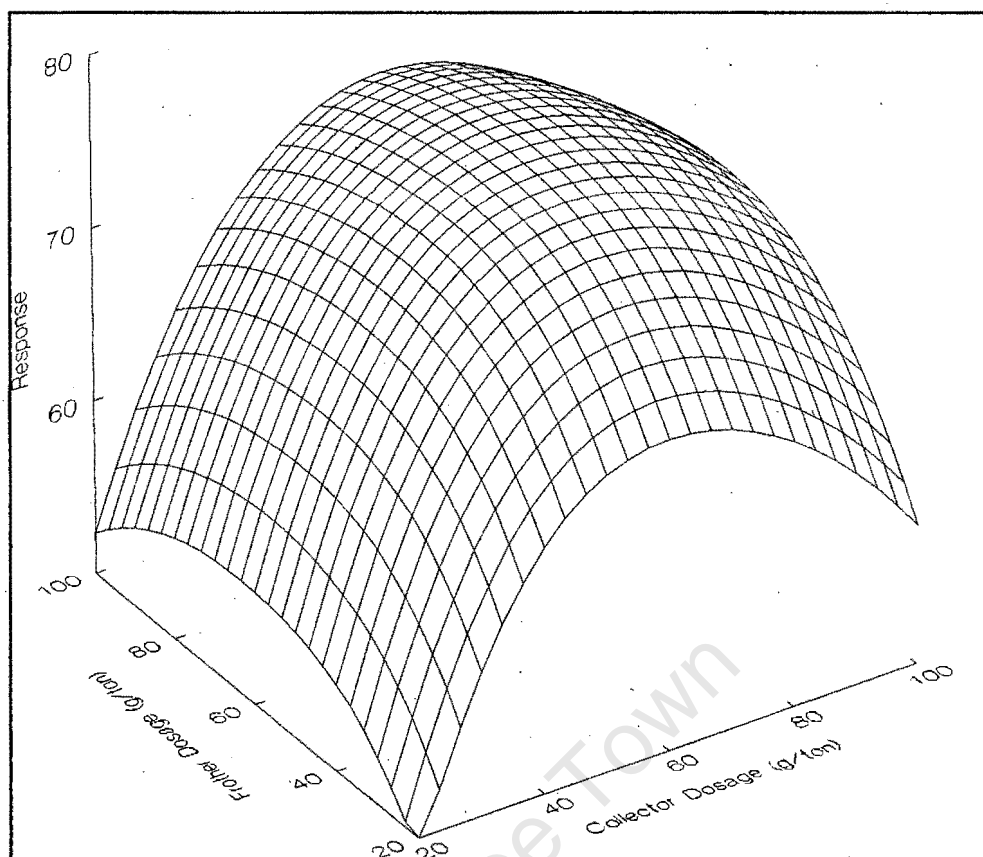


**Figure 4.9** - Pyrite Flotation Yield vs diC3 DTC Collector Dosage (near mono-layer)

far too low. Thus previous work using standard flotation was studied to determine a more appropriate collector dosage. Previous work by the author [Austin and Henwood, 1991] included a factorial design to evaluate the optimum collector and frother doses for a pyrite-sodium dipropyl dithiocarbamate system. The mineral system used was St Helena slimes concentrate and contained 3.5% pyrite. Figure 4.10 below shows that flotation went through an optimum at 80 g/ton of collector. If it is assumed that the collector attached only onto the pyrite, optimum collector dosage is  $3.6 \mu\text{l/g}$  pyrite. This is 20-30 times more than that calculated through mono-layer coverage estimations.

Microflotation tests performed at this concentration gave 83.2% yield. This dosage was still expected to be too high so microflotation yields were determined using fractions of this dosage, as well as at double this dosage. The results are shown in Figure 4.11 below (runs F2, F6, F4, F5, F9, F8 and F10). These tests confirm that the results of Austin and Henwood [1991] are correct for pure pyrite, given the assumption that adsorption takes place on the pyrite surface only. The yield improves linearly from 46.8% at no collector addition to 83.2% at  $3.6 \mu\text{l/g}$  collector addition. Above this dosage, the yield flattens off and doubling the collector dosage results in almost no improvement in flotation



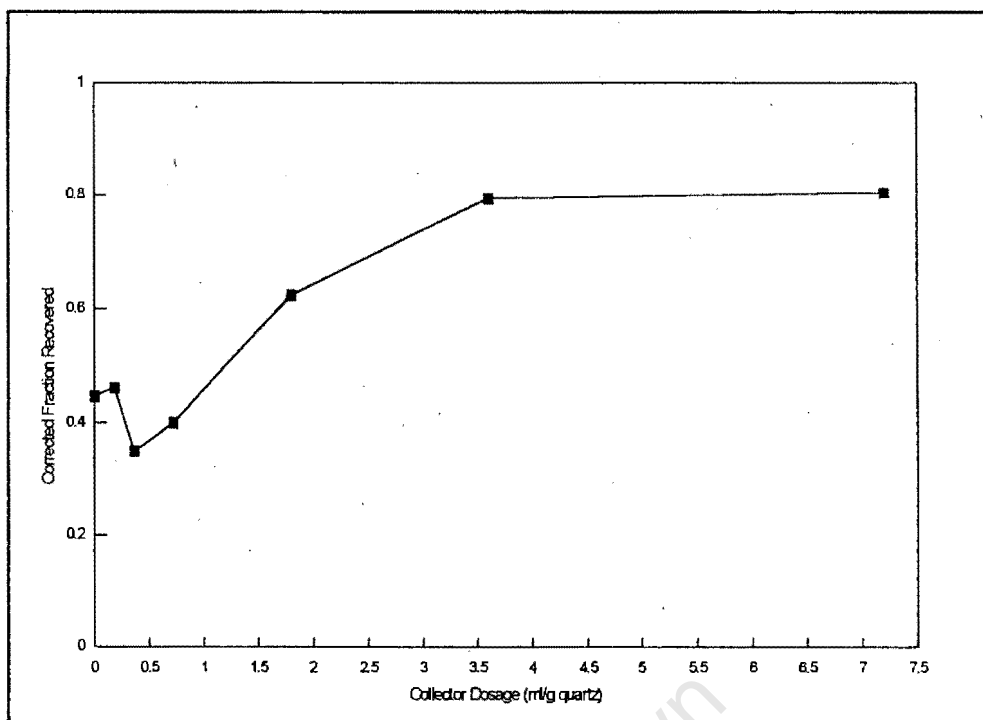


**Figure 4.10 -** Flotation Response for Collector and Frother (from Austin and Henwood, 1991)

yield, which only increases to 84.5% at 7.2  $\mu\text{l/g}$  of collector addition.

This dosage is many times more than that required for mono-layer coverage. Thus, either equilibrium between collector in solution and on the mineral surface is very strongly shifted to the solution phase, or the collector is reacting on the mineral surface or in solution. Exactly what is happening can be determined by analysis of the adsorption curves. This is done in section 4.5.4, below.

An important observation is that for both the quartz-amine system and the pyrite-thiol system, adsorption is linear over a large range. In the case of quartz, this was in the region below mono-layer coverage, while for pyrite, this occurs well above mono-layer coverage. Since all other variables have been kept constant, a definite relationship can be developed between  $P_a$  (probability of attachment) and collector dosage. Assuming that adsorption is proportional to dosage (since an equilibrium is reached) this implies a linear relationship between surface coverage and flotation recovery. This appears to be contrary to previous work, such as Crawford and Ralston [1988], where surface



**Figure 4.11 - Collector Dosage vs Flotation Yield (high doses)**

coverage produced a definite quadratic relationship. Stassen's model assumed direct proportionality between collector dosage and recovery, whereas this shows proportionality, but not direct. This result may be the basis for further investigation, in the future.

Another aspect to note is the initial dip in flotation recovery. While a more in depth study of this is beyond the scope of this thesis, the author postulates that diC3 DTC may display some depressant properties at very small doses. Pyrite at this pH (pH4) is naturally very floatable and small doses of diC3 may negatively affect the surface properties. If diC3 DTC were, for example, to increase the forward energy barrier (of attachment between particles and bubbles), while at the same time increasing hydrophobicity (see Chapter 2 for a discussions on the thermodynamic and kinetic factors of conditioning) these two factors of flotation would have opposing effects on the probability of any particle being floated. The change in floatability would be determined by which factor dominates. It is entirely feasible that the forward energy barrier initially reduces the probability of flotation more than the opposing factor of increased hydrophobicity can increase the probability of flotation. This would lead to the results observed, where flotation initially drops slightly with increasing collector dosage, before increasing toward the optimum dosage (and maximum flotation).

Since the optimum collector dosage, as defined above, has now been determined, all further test work was conducted around this collector dosage of  $3.6 \mu\text{l/g}$ . This translates to  $2.5 \mu\text{moles/g}$ . The equivalent dosage of PNBX (in pure powder form, molar mass  $188 \text{ g}$ ) is  $470 \mu\text{g}$  of PNBX /g of pyrite.

#### 4.5.4 Pyrite-Thiol Adsorption

Preliminary UV absorbency tests were carried out at known collector dosage to determine the optimum wave-length at which to measure the residual collector concentrations for each collector. The results showed peaks for diC3 at  $280 \text{ nm}$  and for PNBX at  $300 \text{ nm}$  respectively. The absorbency measured for this known collector dosage allowed the calculation of the extinction coefficients. Table 4 gives the results for these tests.

Table 4: Thiol Collector Absorbency Values

Collector Type	Collector Conc.	Absorbency Peak	Absorbency	Extinction co-eff.
di-C3	$25 \mu\text{moles/l}$	$280 \text{ nm}$	0.293	11 720
PNBX	$25 \mu\text{moles/l}$	$300 \text{ nm}$	0.392	15 680

Since thiols are notoriously unstable in aqueous solutions, tests were performed to determine the half-life of these two collectors used at pH 4. It was important that the collectors should be stable under the test operating conditions, for adsorption of collector out of solution not to be confused with degradation of the collector. The half-life for xanthate is 90 minutes, while the diC3 is more stable under these conditions, with a half-life of 950 minutes [Bradshaw, 1994]. Since most of the tests took place within 8 minutes of achieving correct pH, degradation of the collector over the conditioning test period was not considered to be a factor in the test work.

It was also necessary to determine the expected absorbency of dissolved solids from pyrite in solution, as well as buffer in solution. This was so as to correct for these values when measuring conditioned solution absorbencies to find residual collector concentrations. The quartz solutions resulted in an extremely high base-line, which swamped any amine values expected at the desired concentrations. Table 5 below shows that this was not the case for pyrite, with

an absorbency of 0.062 for a solution sample taken from a well mixed pyrite-water system. But both pyrite and the buffer did show some absorbency at the peak for collectors. These absorbency values are given in Table 5 below, for "conditioned" pyrite in the absence of collector or buffer, buffer alone (at the concentration to be used - namely 0.5 ml / 400 ml), and pyrite "conditioned" with buffer only.

Table 5: Absorbency of Pyrite and Buffer

	Pyrite Only	Buffer Only	Pyrite and Buffer
Absorbency at 280nm	0.062	0.078	0.086
Absorbency at 300nm	0.004	0.06	0.03

The table shows that for UV measurements in the region of 300 nm, the readings are below the machines level of experimental error and will be ignored. At 280 nm on the other hand, the values are significant and should be taken into account. What is significant is that the buffer and the pyrite do not show an additive absorbency effect, as might be expected of two chemicals which are completely unaffected by one another. The reduced absorbency observed is believed to be the result of redox reactions within the solution. The buffer ionic strength may reduce pyrite dissolution and the pyrite dissolution may shift the buffer to an ionic state which is less UV active. Evidence of these effects is that pH and redox shifts naturally occur when pyrite is mixed with water, implying that the ionic state of the water is changing. Much work has been done on these phenomena by Bradshaw [1994]. With the buffer present, pH shift is still experienced, but to a much lesser extent.

So, while accurate estimation of diC3 DTC adsorption has been made somewhat more difficult, adsorption of PNBX can be measured directly from the drop in absorbency readings. This is because, unlike diC3 DTC, PNBX is not affected by interference at its characteristic wavelength of 300 nm. The measurement problems of diC3 DTC were resolved by analysing absorbency at its characteristic wavelength of 280 nm with and without buffer in:

Final adsorption at STD conditions without buffer = 0.03

Final adsorption at STD conditions with buffer = 0.08

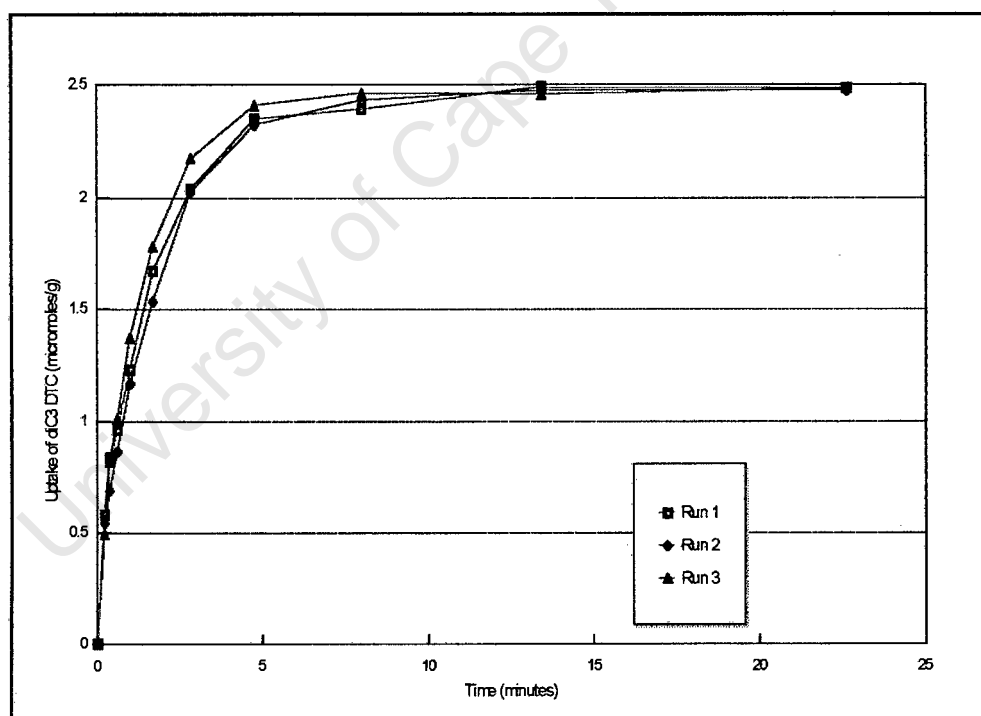
The first value shows that, since final absorbency is lower after adsorption, diC3 DTC suppresses pyrite dissolution. This would be expected, since the mineral surface is covered by collector, obstructing dissolution. Reduced dissolution results in reduced redox impact on the buffer. Thus increased absorbency would be expected, in the case of collector adsorption in the presence of buffer, over a pyrite-buffer mixture. This indeed the case. It is conceivable that some collector remains in solution, but previous work shows that a DTC-metal complex is very stable and has a low ionisation constant, as low as  $10^{-14}$  in the case of nickel complexes [Thorn and Ludwig, 1962]. Thus for the purposes of this work it can be assumed that diC3 DTC adsorbs to completion. Hence the residual UV absorbency will be taken to be the result of buffer and pyrite in solution.

Likewise, a very small interaction between collector and buffer was measured at 280 nm. At standard conditions this resulted in approximately 0.008 less absorbency than calculated through addition of absorbencies. Again this is ascribed to a shift in the ionic state of the buffer. This value is very small, but can easily be accounted for in collector adsorption calculations.

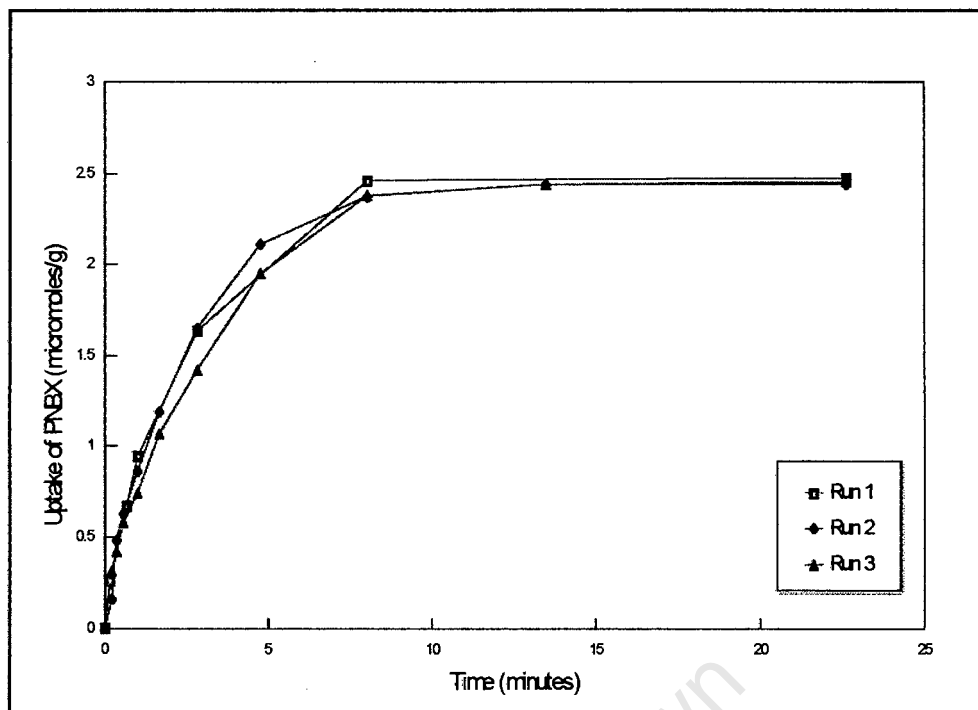
It is important to know that none of the reagents reacts to form new stable products, excepting the collector attached to the pyrite. The phosphate buffer has been used by many researchers in the past [Harris, 1993] and no new product peaks could be found on the UV curve to suggest [Bradshaw, 1994] that any new products are formed.

Knowing that both the initial readings and the final readings of absorbency are affected by pyrite and buffer, it was important to use an effective interpolation scheme to achieve meaningful results. It has been shown by Bradshaw [1994] that the adsorption of collector onto the pyrite surface is well represented by a linear interpolation. It would be unwise to attempt any other form of interpolation, without sound theoretical reasons. The effectiveness of linear interpolation was confirmed by the high linearity of the first order reaction rate fits to the adsorption reaction. This is shown in Chapter 6. While the use of linear interpolation may be challenged, it is important to note that this work is a comparative analysis and consistency of measurement is more important than absolute accuracy.

Preliminary tests on conditioning of the ore were performed at standard conditions, and were repeated to determine the reproducibility of the conditioning and measurement processes. Figure 4.12 and Figure 4.13 show the plots of collector uptake over time, for diC3 DTC (runs 1D, 9D and 12D) and for PNBX (runs 1P, 2P and 3P) respectively, repeated several time for each collector. The shape of the curves will be analyzed in detail in section 6.3. What can be understood from them now, is that the conditioning and measurement procedures are highly reproducible. The standard deviation for diC3 DTC was 0.050 micromoles collector uptake and that for PNBX was 0.051 micromoles. The absorbency error expected of the UV spectrophotometer is in the region of 0.005, which translates to 0.055 micromoles DiC3 DTC and 0.041 micromoles PNBX collector uptake. This is of the same magnitude as the standard deviation for the two standard deviation tests. Therefore, the error can be explained by the measurement error of the UV spectrophotometer. The results achieved are reproducible.



**Figure 4.12 -** Reproducibility Tests Showing Collector Uptake vs Time for DiC3 DTC



**Figure 4.13 -** Reproducibility Tests Showing Collector Uptake vs Time for PNBX

## 4.6 Conclusion

This chapter set about answering three questions. The first was: how will conditioning be measured? The measuring system proposed was two tier. First adsorption studies would be used to directly measure the effect of conditioning on the mineral-collector system. This would be supplemented by the use of microflotation to relate adsorption results to flotation response and hence provide a relationship between conditioning and flotation response. Adsorption studies provide the advantage of directly measuring conditioning effectiveness rather than attempting to infer conditioning effects through measuring the more complex process of flotation. While, microflotation was chosen for measuring flotation response as it eliminated the complicating froth phase, which can mask the conditioning effects. Adsorption was calculated by measuring the loss of collector from solution, using UV spectroscopy.

The second question was: what mineral system will be used? A quartz-amine mineral-collector system was initially chosen, for its simplicity. This was eventually discarded because of difficulties with measuring the very small doses of collector used. A pyrite-thiol system was finally chosen as the system to be used in the conditioning test work. While this is a more complex system, the effects of conditioning could be readily

measured. The results of conditioning pyrite with both diC3 DTC and PNBX as the collector were found to be reproducible.

The third question answered was: what equipment and experimental technique is required? A cylindrical baffled vessel was designed for the conditioning stage. A pitch blade impeller driven by a heidolph variable speed motor was used to agitate the slurry. The impeller design was chosen to allow the power input into the conditioned slurry to be calculated using equation (17) derived by Oldshue [1983]. The microflotation cell used was based on a design by Partidge and Smith [1981]. The experimental procedures for adsorption studies and microflotation studies were standardised to minimise experimental error. The procedures are as follows:

### **General Conditioning Procedure**

- The mineral was prepared, weighed and introduced into the conditioning vessel with the appropriate volume of liquid.
- The stirrer was switched on (at a predetermined rpm).
- The pulp was brought to the correct conditions using acid and buffer.
- Collector was injected into the pulp, near the impeller to maximise mixing speed.
- Timing began at the moment of injection of collector.

### **Adsorption Study Procedure**

- Liquid samples were removed from the conditioning vessel at given times, using a pipette.
- The liquid was immediately forced through millipore filters to remove any solids and hence "freeze" the level of collector in solution.
- The liquid was measured for UV absorbency at the characteristic frequencies for which the chosen collector displayed a peak.



### Microflotation Procedure

- The contents of the conditioning tank were poured into the microflotation cell and additional water was used to clean all ore into the cell, as well as topping up the cell.
- Air was turned on.
- Agitation began.
- As soon as bubbles begin to rise through the glass filter timing began.
- The mineral was floated for 1 minute.
- Agitation and aeration were turned off.
- All floated mineral was collected, dried and weighed.
- Tailings were sometimes weighed to check mass balance, if necessary.

The next chapter discusses the variables of conditioning to be studied and experimental program to be followed.

# **CHAPTER 5 - DEFINING THE EXPERIMENTAL PROGRAM**

## **5.1 Introduction**

Chapter 4 described the investigation which resulted in the choice of the (pyrite-thiol) mineral-collector system to be used in the study of the effect of the variables of conditioning on conditioning effectiveness. The chapter also described the experimental procedures to be used in the conditioning, adsorption and microflotation tests. This chapter covers the choice of variables to be studied in the experimental program, as well as developing an efficient method of testing the effects of all these variables.

Some of the variables included in the program were chosen in order to address questions left unanswered after the analysis of Stassen's work (Chapter 3). The remainder of the tests revolve around the concept of conditioning being a heterogeneous stirred tank reaction, with adsorption as the important reaction. It was hoped that a better understanding of this could lead to better efficiencies of conditioning.

The choice of variables to be studied is discussed in section 5.2 below. The development of the experimental program is presented in section 5.3.

## **5.2 Variables to be Studied**

To date most studies of conditioning have centred on the energy input into the conditioning process. This has been studied both as a function of time and of power. Stassen's work attempted to link these variables and related conditioning effectiveness to energy input. Critical analysis of his work (section 3.8) showed that power and time appeared to affect flotation performance independently of each other and not merely as two components of the same input variable, namely energy. Thus, the first aspect to be studied in this investigation was the relationship between time, power and energy input into the system, to allow Stassen's claim to be either confirmed or refuted.

Industrial experience shows that collector type plays an important role in the flotation of minerals. The choice of collector is often ad hoc and little is known about why

different classes of collector, displaying similar properties, vary in their effectiveness from one complex ore to another. It is expected that the mechanism of attachment plays some role in this variability: this would affect adsorption rates and equilibrium concentrations. Thus, another key aspect of the study was the effect of collector type on its rate of adsorption onto the pyrite surface. From this, reaction mechanisms of adsorption, for each collector, might be deduced. Each of the other variables was studied in terms of its effect when using different collectors.

Owing to the experimental procedure, time was always a tested variable of the system. The taking of regular samples from the same test, over time, greatly reduces the number of experiments required for the study of any combination of variables which includes time. A logarithmical increasing time interval was chosen to maximise the information gained (see section 5.3.2). Power input, on the other hand, could be altered through changing the impeller speed, or the impeller type or size, or by changing the volume of liquid to be conditioned. For this work, impeller speed was chosen as the means of varying power input. Impeller speed strongly affects the shear forces and eddies within the slurry. However, since the conditioning of pyrite [Bhaskar and Forsling, 1991] is thought to be diffusion controlling, varying the power input by changing the impeller speed was expected to influence adsorption rate differently than maintaining the same shear while changing the volume to which it is applied. For this reason, a few tests were run at a constant impeller speed, using different slurry sample volumes. It was hoped that this would indicate whether future work should be performed to investigate more efficient methods of adding power to the slurry. Thus type of power input was also covered by the tests.

The concentration of collector is a vitally important consideration in the flotation of minerals. Too much collector is wasted money, while too little collector results in poor recoveries. The concentration of collector in solution affects adsorption rate in both diffusion and reaction controlling systems; sufficient adsorption for flotation can be achieved more rapidly at high collector doses. This can lead to a trade-off between the cost of additional collector incurred by overdosing and the capital and energy costs incurred by the use of too little collector. A clear understanding of the effect of collector dosage on adsorption rate will facilitate design decisions such as this. Thus dosage of collector was a further variable to be included in the study.

If the adsorption of collector onto pyrite were diffusion controlling, the bulk collector concentration would affect the diffusion gradient, and hence the rate of diffusion. This

implies that any change that increased bulk concentration of collector would improve adsorption rate, e.g. reduction in the water content of the slurry in the conditioning stage of flotation. The reduction in water content would additionally reduce the dissipation of power into water, which is wasted energy. Thus the effect of reducing water content during conditioning was studied, to determine the possible advantages of high pulp density conditioning. Extremely high solids content has problems of its own, including increased viscosity. It was appreciated that this may cause process problems when trying to increase pulp density in some commercial systems, but the tests in this work were still performed at very low pulp densities.

Finally, as the test work progressed it was expected that some of the results obtained would require further investigation, or might uncover some unexpected new area of interest. For this reason, the test work was left slightly open ended to allow expansion into new areas if necessary.

Thus the experimental programme was planned to include the following topics:

- 1) Effect of collector type
- 2) Reaction Mechanisms of adsorption
- 3) Time effects of conditioning
- 4) Power effects of conditioning
- 5) Effect of type of power input into conditioning
- 6) Relationship between time, power and energy input
- 7) Effect of collector concentration on adsorption rates
- 8) Influence of water content on conditioning effectiveness
- 9) Other observed effects

With the variables and topics of study clearly defined, the experimental program of investigation could be developed.

### 5.3. Experiments Chosen

For simple multi-variate analysis of a system, a factorial design is often the most effective and complete way of determining the effects of variables and their interactions. This work, however, was aimed at analysing separate aspects of conditioning. A number of these, such as collector type, are non-continuous variables, while others were included to provide only a qualitative assessment of the effect of the altered variable. Also, factorial design often becomes cumbersome, when more than 4 variables are to be tested. For these reasons a factorial design for the whole test program was not considered; the areas of interest were studied one at a time. Having said this, some variables were studied in a matrix design, to maximise the information gained by studying them together. The tests designed for the areas to be studied are discussed individually below:

#### 5.3.1. Effect of Collector Type

Collector type was studied because it was felt that the adsorption mechanism of different collectors affects their rate and extent of adsorption. Thus adsorption-time plots generated for each of the collectors, would be expected to reveal information on their mechanisms and adsorption characteristics. Two collector types were chosen for the study (see section 4.2.3.2), namely diC3 DTC and PNBX. A third collector, cyclo-hexyl dithiocarbamate (oC6 DTC), was added for comparison purposes (for this part of the work only - owing to the shortage of mineral). To compare the collectors, each was tested at the same dosage, with all other conditions held constant.

How each collector mechanism influences the relative effects of other variables was also tested, by repeating all of the following tests using both diC3 DTC and PNBX collectors.

#### 5.3.2. Time and Power Effects of Conditioning

Previous work [Stassen, 1991; Bulatovic and Salter, 1989] has shown that 5-10 kWh/ton ore provides the optimum energy input for flotation. While the present system varies greatly from those described in the literature, the

consistency of this as the optimum for the other systems suggested that 5-10 kWh/ton would be a good mid-point for this work. The only change is that the present experiments were carried out at very low pulp density and thus power is reported in terms of kWh/ton *slurry*, with the desired mid-point at 10 kWh/ton.

One further constraint was the minimum stirrer speed for adequate suspension of solids in the slurry. Pyrite has a high density and thus good mixing of pyrite throughout the conditioning vessel could not be achieved without very vigorous agitation. But since suspension of the solids off the vessel floor was all that was required, it was found that a minimum impeller speed of approximately 390 rpm could be used.

With these starting values, an experimental matrix was developed to maximise the information that would be obtained regarding the relative importance of power and time, and their implications on energy input calculations. This was best achieved by using power and time values which give equivalent energy input. Thus, for any given level of energy input, a number of permutations of power and time were selected, allowing easy comparison of their relative importance. The matrix shown in Figure 5.1 below illustrates the idea, which also minimised the number of tests that needed to be performed. By choosing exponentially separated test points, it was possible to generate iso-energy lines which intersect the test points, as in the Figure. The Figure also shows that a 4x4 level matrix will give 7 energy levels, of which 5 will have more than one combination of power and time.

This system may be difficult to understand without comparing values along an iso energy line. Consider the energy line beginning at 1 time unit and  $n^2$  power units. This corresponds to energy =  $1 \times n^2 = n^2$ . Moving down the energy line to the next point, gives energy =  $n \times n = n^2$ . Likewise the final energy value is also  $n^2$ . This is true for all of the energy lines. This system provides two useful features, the first of which has been demonstrated to be iso-energy levels, while the second is to provide an exponential set of points for variables which are known to provide exponentially diminishing returns.

The magnitude of the coefficient  $n$  for the exponent determined the range of energy over which the extent of conditioning was tested. Stassen chose an

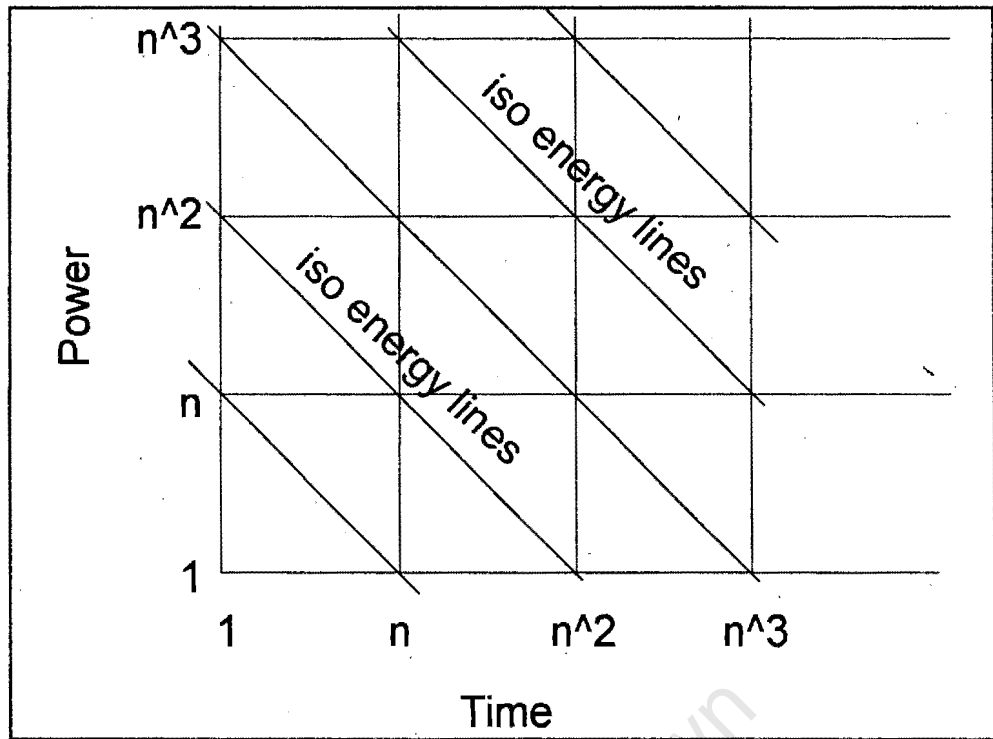


Figure 5.1 - Experimental Design Matrix

energy range of 0.1 kWh/ton to 100 kWh/ton, which is a range of three levels of magnitude. Given that the minimum energy tested for the present system was  $x_{\text{time}} \cdot y_{\text{power}}$ , the maximum energy tested would equal  $n^6 \cdot x \cdot y$ . Using  $n=2$  gave the maximum energy tested = 64 times the minimum tested, while  $n=3$  gave 729 times the minimum. An analysis of how power input is calculated helped to choose the most convenient value for  $n$ .

As given before, Oldshue [1983] has shown that for any particular impeller design, a dimensionless power number can be found, which is constant for a given Reynolds number. This power number relates impeller diameter, rpm and power input into the system. This equation is as follows:

$$N_p = \frac{2.158 \times 10^{17} P}{N^3 D^5 \rho} \quad (17)$$

The axial flow impeller chosen has a constant  $N_p = 1.27$  for all  $N_{Re} > 100$ . Thus for a given diameter and pulp density, any desired power input can be achieved by altering the impeller speed. This is shown in the function below (previously given in section 4.4.1.2).

$$N = \sqrt[3]{\frac{2.158 \times 10^{17} P}{N_p D^5 \rho}} \quad (22)$$

For a desired energy input of 10 kWh/ton into 400 ml of solution of S.G.≈1 over say two minutes duration:

$$P = 3.333 \times 10^{-2} \text{ W}$$

$$N_p = 1.27$$

$$D = 40 \text{ mm}$$

$$\rho = 1$$

Using equation (22),  $N = 381 \text{ rpm}$

This corresponds approximately to the minimum impeller speed to keep the solids in suspension of 390 rpm. Equation (22) also shows that doubling the impeller speed results in an 8 fold increase in power number. Thus, if the impeller speeds to be used are 390 rpm, 500 rpm, 707 rpm and 1000 rpm, the power input of each impeller speed will be equal to  $2^{3/2}$  times the previous ( $n=2^{3/2}$ ). This gives a maximum power input of 22.6 times the minimum power.

Likewise times were chosen that fitted the iso-energy grid. It was found more practical to use one minute as the time basis from which to calculate the rest of the testing times. Since extra test points required no extra tests, it was thought prudent to add intermediate points to aid further analysis of the data. The increment is  $2^{3/4}$  times the previous value. Hence the following testing times were used: 12 s, 21 s, 1 min, 1 min 41 s, 2 min 50 s, 4 min 45 s, 8 min, 13 min 27 s, 22 min 38 s.

These combinations correspond to an energy input range of approximately 1 - 500 kWh/ton.



### 5.3.3. Effect of Type of Power Input (Volume)

This test was intended as a qualitative analysis of the potential for optimising the method by which power is input into a slurry. This test involved using the same equipment and impeller speeds, but reducing the quantity of slurry conditioned by half from 400 ml to 200 ml. This approximately doubled the energy input per unit volume, without affecting the shear applied near the impeller.

### 5.3.4. Collector Concentration

Collector concentration has already been shown, in Chapter 4, to involve some interesting effects. In section 4.5.3 mono-layer doses of collector were seen to have almost no effect on flotation. The reason for this needed to be investigated. The rate and extent of depletion of collector from solution at higher doses was another important area of investigation, to determine how rapidly equilibrium was reached and what this equilibrium value was. The effect of increasing and decreasing this concentration on adsorption rate and extent was also investigated.

Conditioning tests were performed at mono-layer dosage of collector and at doses corresponding to half and double the standard dosage of  $3.6 \mu\text{l/g}$  pyrite.

### 5.3.5. Water content

The investigation of the effect of increasing the pulp density in the conditioning vessel to improve diffusion and power input, comprised one test at standard conditions (given below), except that the water content of the slurry was halved. This differed from section 5.3.3 above in that the above experiment involved halving all components of the slurry, while in this test the collector and mineral content were maintained at the standard quantities ( $3.6 \mu\text{l/g}$  pyrite of collector and 4 g of pyrite).

## 5.4. Summary of Tests to be Performed

The conditions chosen as standard, and against which all parameter changes were measured were as follows:

impeller speed	=	500 rpm
diC3 DTC collector concentration	=	3.6 $\mu$ l / g pyrite
PNBX collector concentration	=	
Buffer dosage	=	0.5 ml
Liquid volume	=	400 ml
pyrite mass	=	4 g

A number of standard run have already been analyzed in Chapter 4, to determine reproducibility for the adsorption technique. The following table provides a summary of the remainder of the experimental program:

Variable Tested	Conditions to be varied from STD
Collector Type	use 3 collectors: diC3 DTC, PNBX and oC6 DTC
Power Effects	impeller speeds of 390, 500, 707, 1000 rpm
Time Effects	Every run was sampled at the times given in 5.3.2
Type of Power Input	one test where every slurry component was halved
Collector Concentration	collector concentration at 1/2 and 2x STD
Water Content (Pulp Density)	one test using half the liquid volume

The next chapter provides a detailed discussion of the results achieved in these tests.

## **CHAPTER 6 - RESULTS AND DISCUSSION**

### **6.1. Introduction**

The results of the experiments performed are discussed in this chapter in logical order, using the topics set out previously in section 5.2. The data are presented graphically in most cases, to facilitate ease of interpretation. The work was carried out according to the procedure described in section 4.4.2. The full details of every test run is given in Appendix F. The results of these tests are discussed in terms of: 1) what was observed, 2) how this relates to predictions made by literature and finally 3) the impact this has on industry.

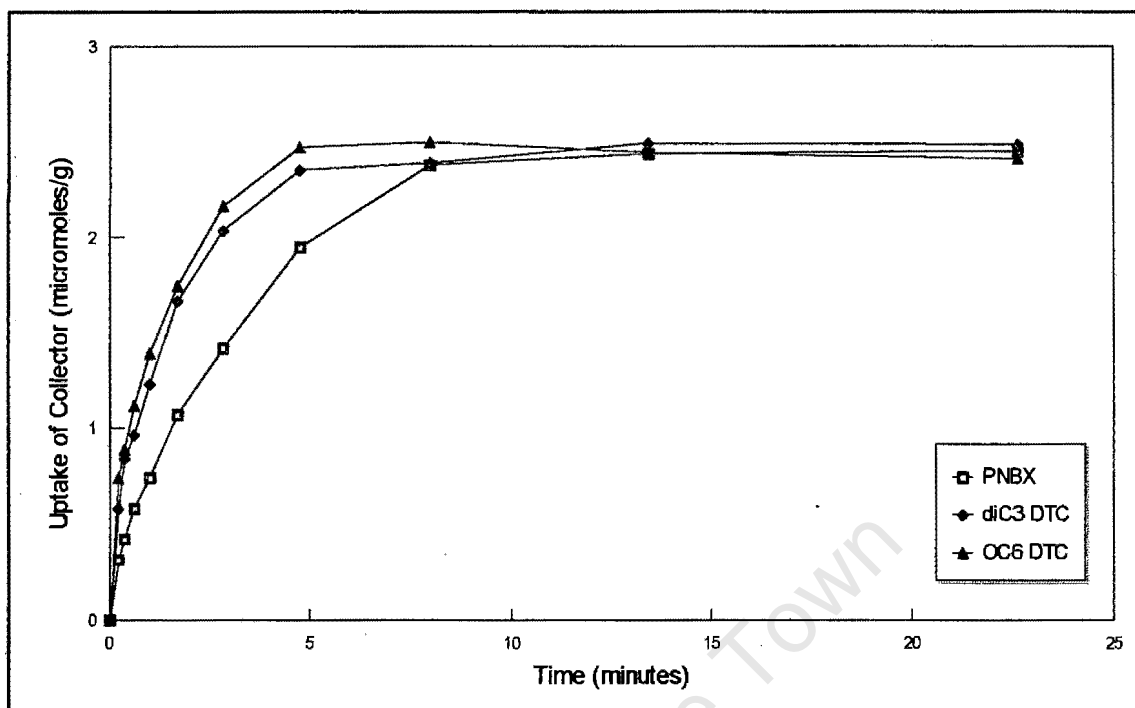
Time and power input are naturally the most important variables to examine, since this whole work carries through it the theme of power and time vs energy input. But first the discussion will cover the theme of collector type. Since the test program for each variable was essentially repeated on each of two collectors, it is useful to determine any characteristic differences between the collectors at this point.

### **6.2. Effect of Collector Type**

To determine the effect of collector type on conditioning, the adsorption rates of the two chosen collectors, PNBX and diC3 DTC were compared with each other at standard conditions. A third collector, cyclic C6 dithiocarbamate (oC6 DTC) was added to this comparison, to provide additional data. As a dithiocarbamate, it was expected to show similar trends to diC3 DTC, but with different adsorption rates, owing to different diffusivity and surface charges.

The tests were carried out at standard conditions. The results appear in Appendix F, runs 3P, 1D and 5D. In Figure 6.1 the adsorption of each collector onto the pyrite surface is plotted as a function of time. As may be seen, all of the collectors adsorbed very rapidly onto the pyrite surface, with equilibrium adsorption reached within approximately 10 minutes of injection into the slurry. The most rapidly adsorbing collector was oC6 DTC, followed in turn by diC3 DTC and PNBX. The most

important observation here is that PNBX adsorbs substantially more slowly than do the DTC's.



**Figure 6.1 - Adsorption Profiles of Three Thiol Collectors**

In laboratory scale batch flotation tests on pyrite samples, using collectors of equal alkyl chain length (the hydrophobic tail), it has been noticed that xanthates repeatedly outperform dithiocarbamates in mineral recovery [Bradshaw,1992]. Taken together with the adsorption profiles observed in Figure 6.1 this would imply that despite increased adsorption, the DTC's work far less efficiently than do xanthates. There is a plausible explanation for this, and it involves conditioning.

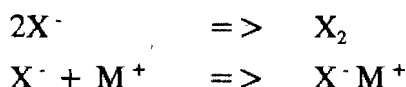
Laboratory scale batch flotation is a high intensity process, with very good mixing within the cell, as demonstrated by calculations of the power input for the flotation cell used by Stassen (section 3.6). Typical impeller speeds are around 1500 rpm, and the power numbers of most batch flotation cells exceed 5, being Rushton turbines or similar radial flow impellers. (The present system uses 500 rpm impeller speed and has a power number of 1.6). Thus the 10 minutes of flotation time typically employed by Bradshaw [1992] was more than adequate for conditioning to reach completion. At equilibrium, all the collectors are equally adsorbed (c.f. Figure 6.1). Thus the difference in collector efficiency of the collectors is the result of their differences in their chemistry alone, and is not influenced by their rates of adsorption.

Nonetheless, while the PNBX is a more effective collector, the DTC's adsorb more rapidly. It is conceivable that there is a level of conditioning such that the DTC's provide better flotation by virtue of their increased adsorption level. This result can be likened to the R-k trade-off, described by Klimpel [1984] for flotation recovery. In this case, there would be a trade-off between rate of adsorption and the effectiveness of the particular collector adsorbed. Thus, the choice of whether to use a xanthate or a dithiocarbamate collector might be determined by the initial extent of conditioning. Since mixing in an industrial flotation cell is far poorer than in the small, well mixed conditioning vessel used in these tests, this effect would be expected to be far more pronounced on a plant (this would depend on whether the 'R-k cross-over' has been reached or not). It is therefore recommended that plant tests be carried out to determine whether or not this observation might be used to advantage when conditioning resources are limited. Increases in plant throughput may for instance result in limited conditioning time.

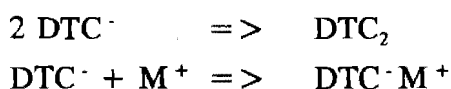
Having observed the different profiles for a xanthate collector and two dithiocarbamates, it would be useful to know if this behaviour could be explained by mechanistic theory. The next section discusses how this observation fits the reaction mechanisms believed to occur.

### 6.3. Reaction Mechanisms of Adsorption

The literature cited in section 4.2.3.2 presents two reaction mechanisms for xanthate and dithiocarbamate adsorption onto a sulphide mineral. There are numerous other reactions that both collectors can undergo, but at this pH, the following reactions are most likely to occur on the mineral surface:



and



Thus both collectors either attach to the mineral in an ionised form, or they utilise the mineral as a reaction site to form dixanthogen or DTC<sub>2</sub>. Which of these two products is formed by each collector is strongly determined by the pH and the sulphide mineral type.

At pH 4 in the presence of pyrite, dixanthogen is the dominant xanthate product. Dixanthogen is insoluble in water and hence the surface reaction of  $\text{PNBX} \Rightarrow \text{PNBX}_2$  effectively precipitates PNBX out of the solution. Thus, provided there is pyrite present to provide the reaction site, xanthates will continue to react until the solution is totally exhausted of any xanthate. Dithiocarbamates, on the other hand, remain ionised on the pyrite surface and are hence reversibly attached to the mineral. This results in the formation of an equilibrium between DTC's on the mineral surface and in solution, though this equilibrium value is very small [Thorn and Ludwig; 1962].

The formation of insoluble dixanthogen is a slower reaction than simple ionic attraction, and the presence of the dixanthogen may inhibit the rate of electron transfer, necessary for further adsorption and dixanthogen formation. This would result in a slower adsorption of xanthate than dithiocarbamate onto pyrite. Figure 6.1 shows exactly this effect. Hence the mechanisms which have been proposed by the literature are supported by the results of the adsorption tests.

It was noted in section 4.5.3 that the diC3 DTC collector dosage was substantially in excess of that required to provide a mono-layer coverage of the pyrite surface. Tests also showed that the collector did not react with the buffer and was relatively stable over the time period of the conditioning tests. This would suggest that the collector must adsorb to the mineral surface in multi-layers. This multi-layer adsorption was also observed by Bhaskar and Forsling [1991] who state that xanthate was observed to adsorb "up to 80 mono-layers" on the pyrite surface.

Conditioning with small amounts of collector (runs 15D and 4P, in Appendix F), results in extremely rapid adsorption which goes to extinction. If the adsorption were even, this would imply that the mineral was almost completely covered by collector. Yet flotation was shown to be poor (section 4.5.3). It is not known exactly why large excesses are required to provide good flotation of pyrite. The mineral surface is known to be highly irregular, with some sites more active than others in the adsorption of collector [Harris, 1993]. It is possible that collector attaches preferentially onto the strong sites, even forming multi-layers in these regions. Thus low doses of collector would attach only in very few sites on the mineral surface, not adequately increasing the hydrophobicity of the mineral. Larger doses, on the other hand, may allow less active sites with the increased adsorption time and overall greater driving force available to adsorb collector, increasing overall surface coverage. It may be necessary

for both weak and strong sites to be coated with collector before sufficient hydrophobicity is achieved for good flotation recovery.

This is largely speculative, yet it does have foundation in literature and experimental observation. More important than the speculated mechanisms, however, is understanding how conditioning and collector type are linked. Understanding the conditioning requirements of the collectors used improves the effectiveness with which they can be utilised in industrial applications.

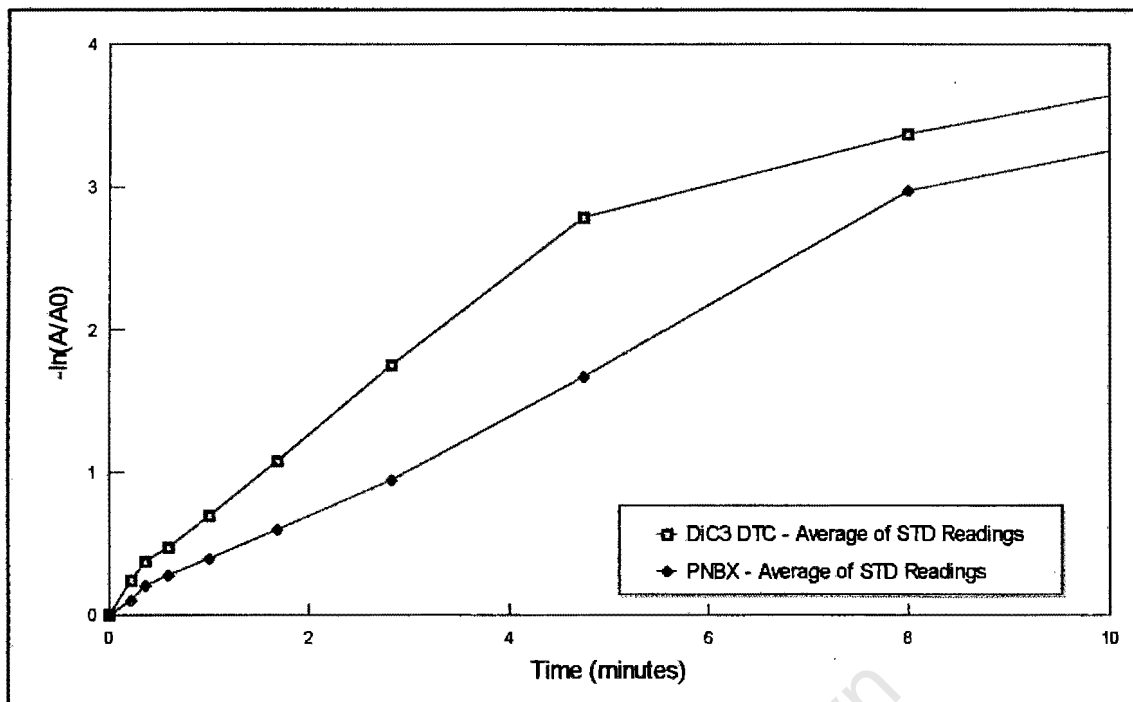
#### 6.4. Time Effects of Conditioning

Conditioning has already been measured as a function of time. The adsorption of collector was plotted against time to give the adsorption profiles of the three collectors (PNBX, diC3 DTC and oC6 DTC) shown in Figure 6.1. The Figure show that conditioning is very rapid, with 50% of the collector adsorbed onto the mineral surface within the first minute of conditioning. Adsorption is complete within 10 minutes of beginning.

It would be useful to be able to determine the reaction order to gain a better understanding of the reaction mechanisms. Also, it is important to measure the rate of the adsorption reaction in order to be able to make quantitative comparisons of conditioning rates at different conditions, as well as comparing different collectors. The same data as given in Figure 6.1 plotted as  $\ln[A/A_0]$  vs time, where  $A$  is collector concentration in solution and  $A_0$  is initial collector concentration, allows calculation of the reaction order and the rate of reaction. This is plotted for diC3 DTC and for PNBX at standard conditions in Figure 6.2.

The Figure shows that the relationship is linear up to the point where collector in solution approaches exhaustion (at approximately 5 minutes for diC3 and 8 minutes for PNBX). A linear regression of the first eight points gives an  $R^2=0.977$  for DiC3 DTC, a good fit which confirms statistically that the relationship is most likely linear. The fit is even better for PNBX, where  $R^2=0.997$ .

A linear relationship between  $\ln[A/A_0]$  and time shows that the reaction is first order in collector concentration. The slope of the line is the rate constant for adsorption of collector onto the mineral surface. This slope was calculated as being  $0.569 \text{ min}^{-1}$  for



**Figure 6.2** - Log of Collector Uptake vs Time for DiC3 DTC and PNBX

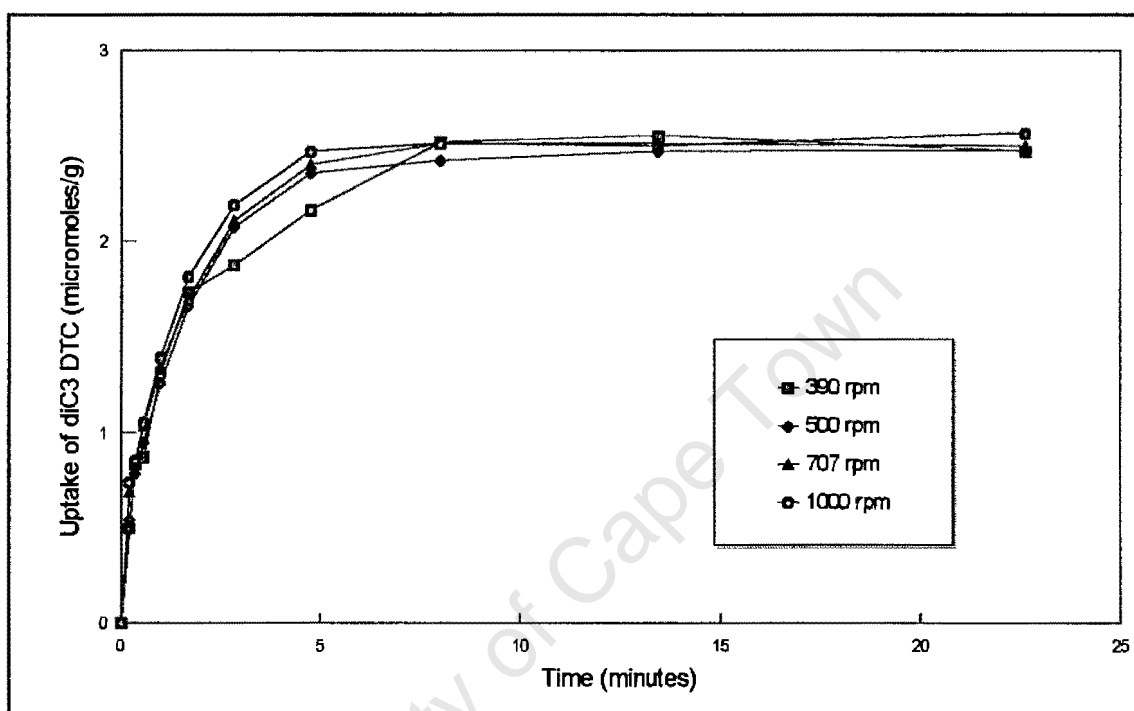
DiC3 DTC and as  $0.338 \text{ min}^{-1}$  for PNBX. This is a relatively large value for heterogenous reactions. The linear relationships with time, and the large rate constants, for both collectors shows that time is an important variable of the conditioning for these collectors.

## 6.5 Power Effects of Conditioning

The effect of power on conditioning was measured by varying the impeller speed during conditioning, while keeping all other variables constant at the standard conditions. The impeller speeds were chosen in Chapter 5 to maximise the information available for comparing the the relative effects of power and time, which is covered in more detail in section 6.7. The impeller speeds chosen were 390 rpm, 500 rpm (standard speed), 707 rpm and 1000 rpm. Each of these increments represents an increase in power of  $\sqrt{8}$  over the previous power see section 5.3.2). All of the impeller speeds were tested using diC3 DTC, but analysis of these results showed that there was no point in doing the same for PNBX, so PNBX was only tested at 500 rpm and 1000 rpm. The data from these tests can be found in Appendix F (runs 2D, 3D, 8D and the average of 1D, 9D and 12D for diC3 DTC; and runs 6P and the average of 2P and 3P for PNBX).

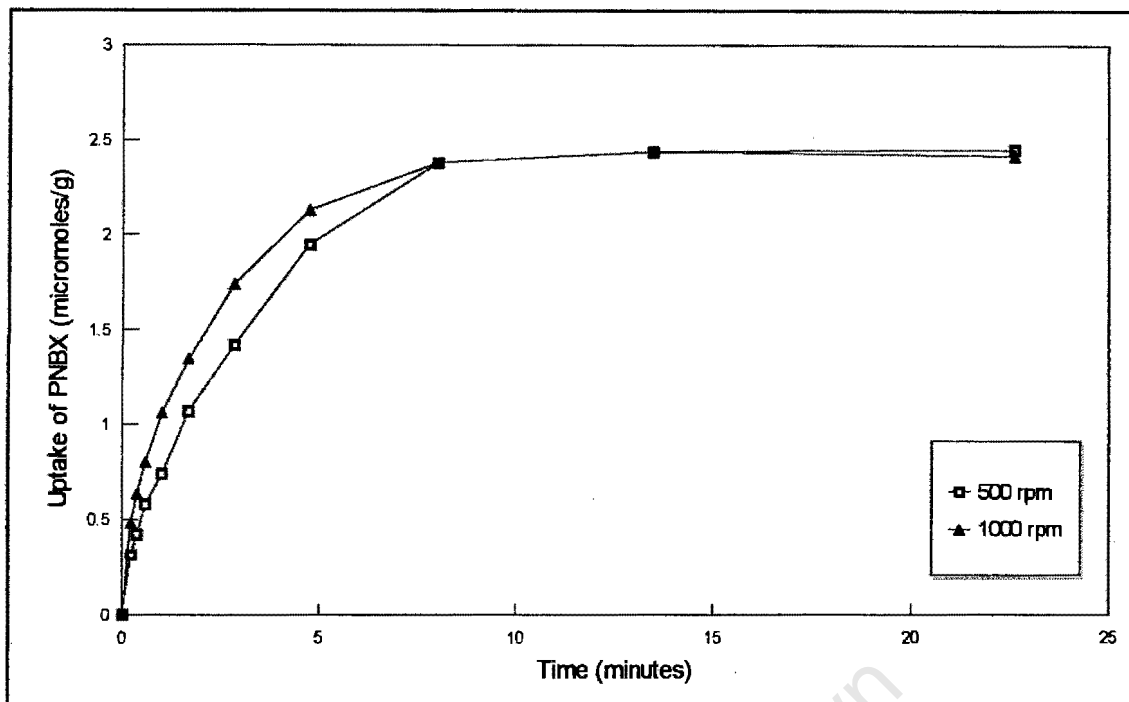


Figure 6.3 and Figure 6.4 show the collector uptake curves at various impeller speeds for diC3 DTC and PNBX respectively. It may be seen that for both collectors there was a small increase in rate of adsorption of collector when the impeller speed was increased to 1000 rpm from the standard speed of 500 rpm. For diC3 DTC, the lower impeller speed of 390 rpm yielded erratic results, which are believed to have been caused by poor mixing of the mineral in the vessel, while the results at 707 rpm fell between those at 500 and 1000 rpm.



**Figure 6.3 - Effect of Impeller Speed on diC3 DTC Adsorption**

From Oldshue's [1983] equation of power number, power input is proportional to the cube of the impeller speed (see eqn 18, section 3.6). Therefore, doubling the impeller speed, from 500 to 1000 rpm, results in 8 times the power input into the system. For diC3 DTC the increase in adsorption after 100 seconds of conditioning time, in going from 500 to 1000 rpm, was in the region of 9%, while for PNBX the increase was approximately 19%. This must be seen against the equivalent increase in energy added by increasing conditioning time rather than power input; where adsorption of diC3 DTC is 50% higher, while adsorption of PNBX is 110% higher. In both cases the influence of time is 5 fold that of power input. Referring to Figure 2.10 of the literature section, one may conclude that conditioning is no longer strongly affected by agitation intensity. This implies that adsorption has moved (or is moving) out of the regime of diffusion control, to that of a reaction controlled mechanism. The small increase in adsorption rate, with increase in power input, shows that diffusion is still slightly limiting. Most literature states, to the contrary, that the reaction between thiol collectors and pyrite is



**Figure 6.4 - Effect of Impeller Speed on PNBX Adsorption**

diffusion controlling [Bhaskar & Forsling, 1991; Crozier, 1993]. Despite this, the result is not unexpected, since the test system was small-scale and hence well mixed. A vessel of the scale used commercially typically has a very low power input and is poorly mixed, resulting in the system being diffusion controlling.

## 6.6 Effect of Type Power Input

This test involved reducing the contents of the conditioning vessel by half; the volume of liquid from 400 ml to 200 ml and mass of pyrite from 4 g to 2 g. The collector addition was also halved in order to maintain dosage at  $2.5 \mu\text{moles/g}$ . This was done in order to ascertain the effect of increased power input without changing the maximum shear forces in the system. The halved volume results in almost double the power input per unit volume of the slurry (and hence unit mass of pyrite). However, the power number changes only very slightly as a result of reduced distance between the surface and the impeller; the change is insufficient to affect the results.

Figure 6.5 shows the adsorption curves for both standard conditions (average of runs 1D, 9D and 12D) and for the system using a halved sample volume (run 4D), using diC3 DTC as the collector. The previous section indicated that little change could be expected for increased power input into the system. This is confirmed by the figure.

There is no measurable difference between the two curves. It may be concluded that it is not possible, using this small system, to perform more detailed analysis of the effect of power type. This does not rule out the possibility that the method by which power is introduced can affect adsorption. But, in order to achieve measurable differences in adsorption rate, a larger, poorly mixed vessel must be used. A plant scale flotation system may prove more revealing.

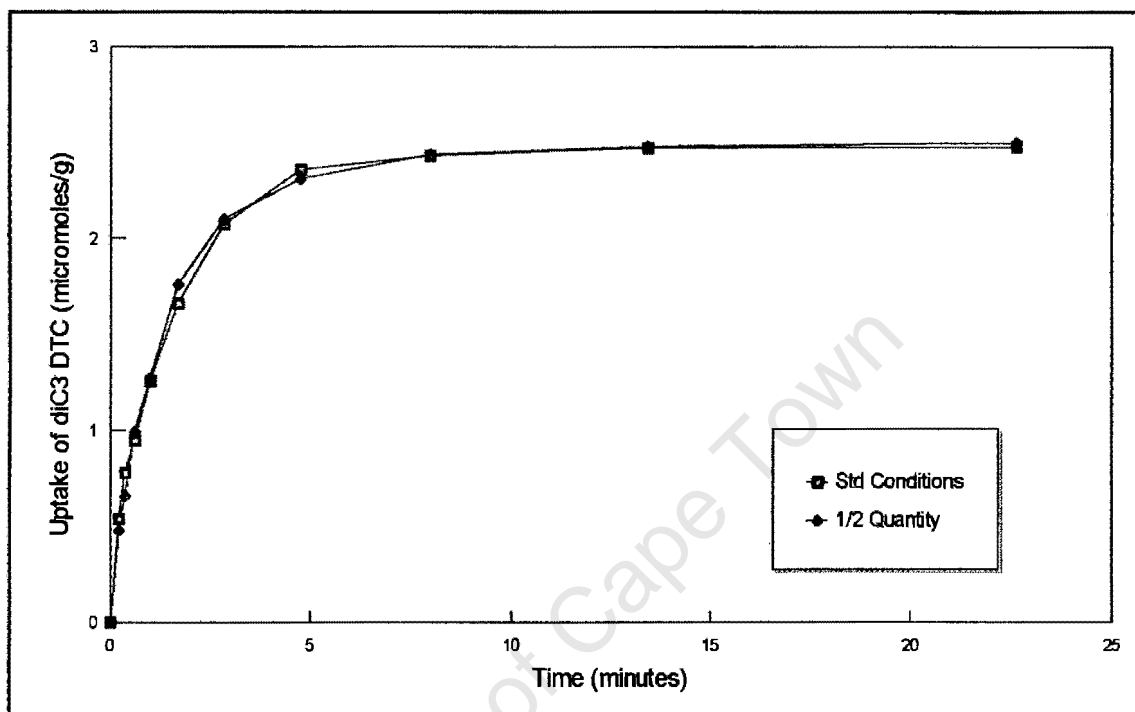


Figure 6.5 - Effect of Power Type on DiC3 DTC Adsorption

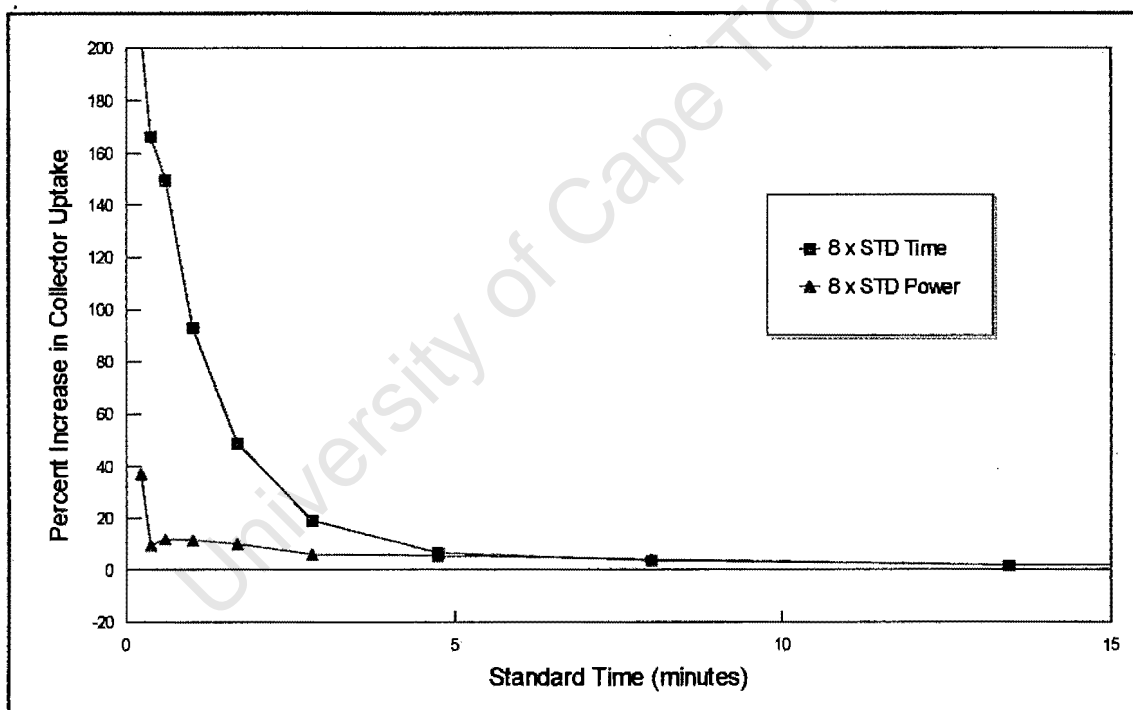
## 6.7 Relationship between Time, Power and Energy

Stassen [1990] hypothesised that the relationship between time, power and energy input into conditioning was a simple one, with energy input being the independent variable affecting the mineral flotation rate and recovery. The implication of this is that it is unimportant whether energy is added using extended conditioning times or high impeller speeds.

The present work has shown that for the pyrite-thiol systems studied (the same kinds of system that Stassen used), this is untrue. Increasing power input into the system has only a small effect on collector uptake by the mineral, while conditioning time has a marked effect on collector uptake, up to 10 minutes. In section 6.5, it was shown that

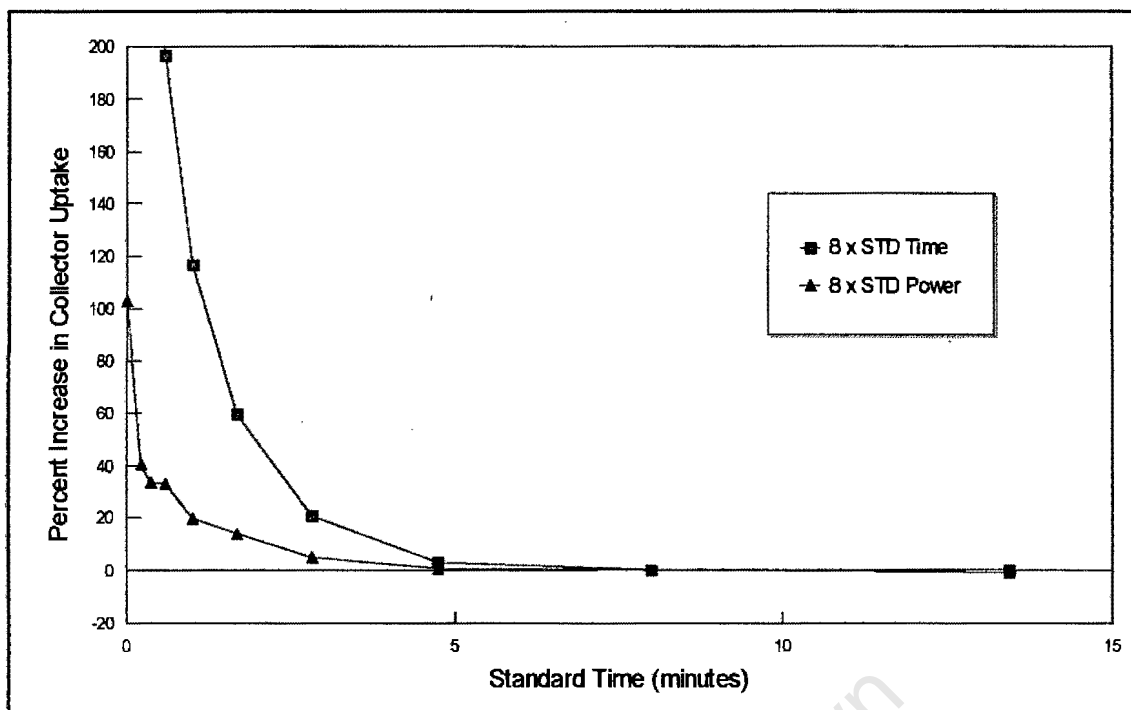
the reaction is first order in time and that time is the dominant variable in the adsorption process. It can be deduced that this system is reaction rate controlling.

Figure 6.6 and Figure 6.7 show the percentage improvement in adsorption for 8 times increase in energy input, using diC3 DTC and PNBX respectively. The additional energy is added as power or as time, and is plotted against standard time in minutes (see Figure 6.3 and Figure 6.4). The addition of 8 times the energy using power is achieved by increasing the impeller speed to 1000 rpm (runs 2D and 6P), while the addition of 8 times the energy as time is achieved by conditioning normally (i.e. at 500 rpm) for 8 times the duration (average of runs 1D, 9D and 12D and average of runs 2P and 3P). The figure shows that adding extra energy as power resulted in hardly any improvement in adsorption, while adding extra energy by agitating for a longer period at the same rpm provides a very large initial increase in collector uptake, approaching 0% as adsorption approaches completion.



**Figure 6.6** - Effect of Eight Times Energy Input using DiC3 DTC

The dominance of time effects over power effects in conditioning is expected to be very different for large, poorly mixed systems. In fact, analysis of Stassen's data (section 3.8) showed that power input was the more important variable for his test system. The point to be made, however, is that power and time are *independent variables*. Using various combinations of these, which correspond to the same total energy input, results in different adsorption or flotation responses. Thus Stassen's observation that energy input is the variable that determines flotation response is incorrect. There may be some



**Figure 6.7 - Effect of Eight Times Energy Input Using PNBX**

regimes where power input and time input are equally effective in improving flotation performance, but the phenomenon would be coincidental, rather than the result of some universal and fundamental law.

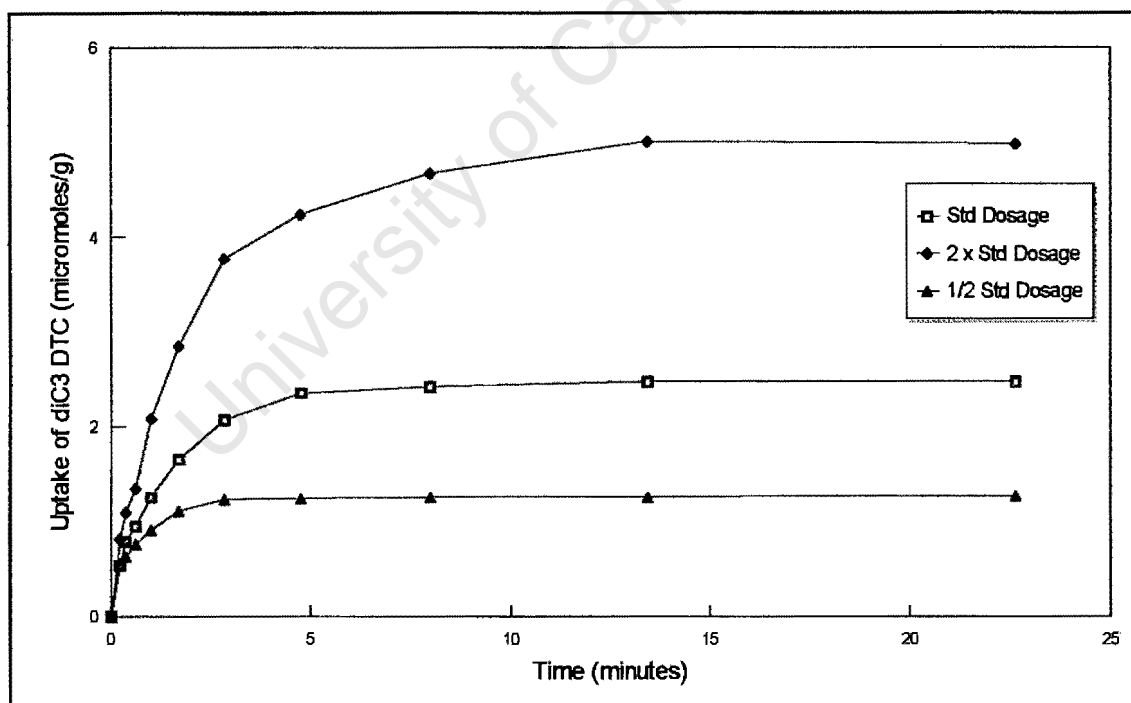
Boundary layer theory, which predicts the effects of turbulence in a stirred system on the diffusion layer thickness of and hence rate of diffusion to, the mineral surface, is very complex [Welty, Wicks and Wilson, 1984]. The theory shows the size of the boundary/laminar layer to be a function of many variables, including system geometry, viscosity, type of turbulence, shear rates, and the magnitude of eddies. These cannot be explained by use of simple energy input functions. Certainly, diffusion rate cannot be linearly related to power input, as would be required for energy to describe flotation responses effectively.

The present work shows that power and time are independent and that Stassen's abbreviated function for energy effects on conditioning should be discarded. What may also be inferred from Figure 6.6 and Figure 6.7 is that energy as a process cost can be minimised for any given required adsorption, by manipulating the combination of power and time inputs. For this system, long conditioning times at low power would be the most energy efficient way of achieving optimum adsorption. In a continuous process, this extended conditioning time must be weighed against the increased equipment cost of larger equipment required to provide the time or volume. This is covered in more detail in the next section.

## 6.8 Effect of Collector Concentration

The effect of collector concentration was studied by conditioning the pyrite using varying doses of collector, while keeping all other variables constant at the standard conditions. Figure 6.8 shows the collector uptake profile as a function of time, for three initial diC3 DTC collector doses (runs 6D, 11D and the average of 1D, 9D and 12D), while Figure 6.9 shows the same details for PNBX (runs 4P, 5P and the average of 2P and 3P).

In Figure 6.8 doses of diC3 DTC are the standard dose, double this and half this dosage. The Figure shows that collector uptake to the pyrite surface is strongly affected by collector concentration. The two elements of each adsorption profile to note in Figure 6.8 are the rate of adsorption and also the final extent of collector uptake. The graph shows that for higher collector doses, the initial reaction rate is higher, and the extent of adsorption is higher. Likewise, the half-standard dosage resulted in reduced rate of collector uptake and a lower equilibrium uptake.



**Figure 6.8** - Effect of Collector Dosage on DiC3 DTC Adsorption

For the PNBX, it was decided to stretch the range of the dosages to 10 x STD and 1/4 of STD to determine if any unusual effects might be observed. The results were very interesting (Figure 6.9). The reduced dosage showed much the same trend as for DiC3

DTC, with the adsorption curve substantially lower than for standard conditions. At 10 x STD dosage, agglomeration of the collector was seen to occur. This has much the same effect as micellation, where the collector is not readily available for adsorption and is wasted. The adsorption test showed a very rapid removal from solution, followed by a slow continuous removal. It was believed that this was caused by attachment of the agglomerates to the container walls and to the pyrite particles. The agglomerates could then slowly spread over the pyrite surface, greatly reducing the rate of removal of collector from solution.

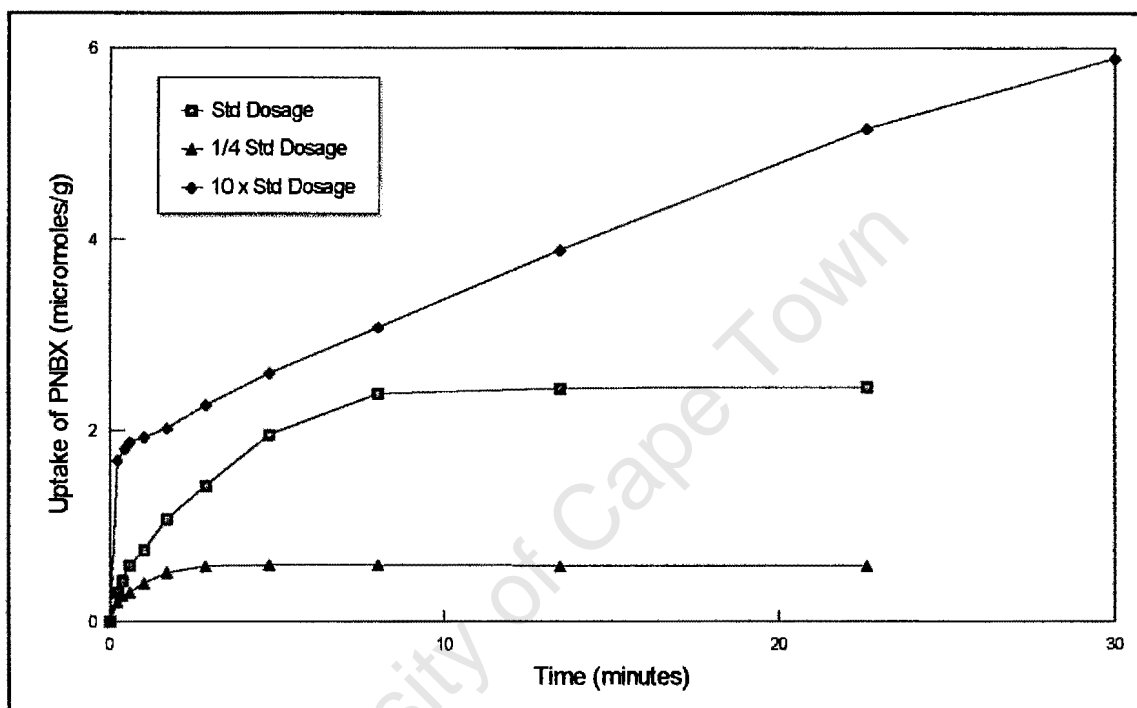
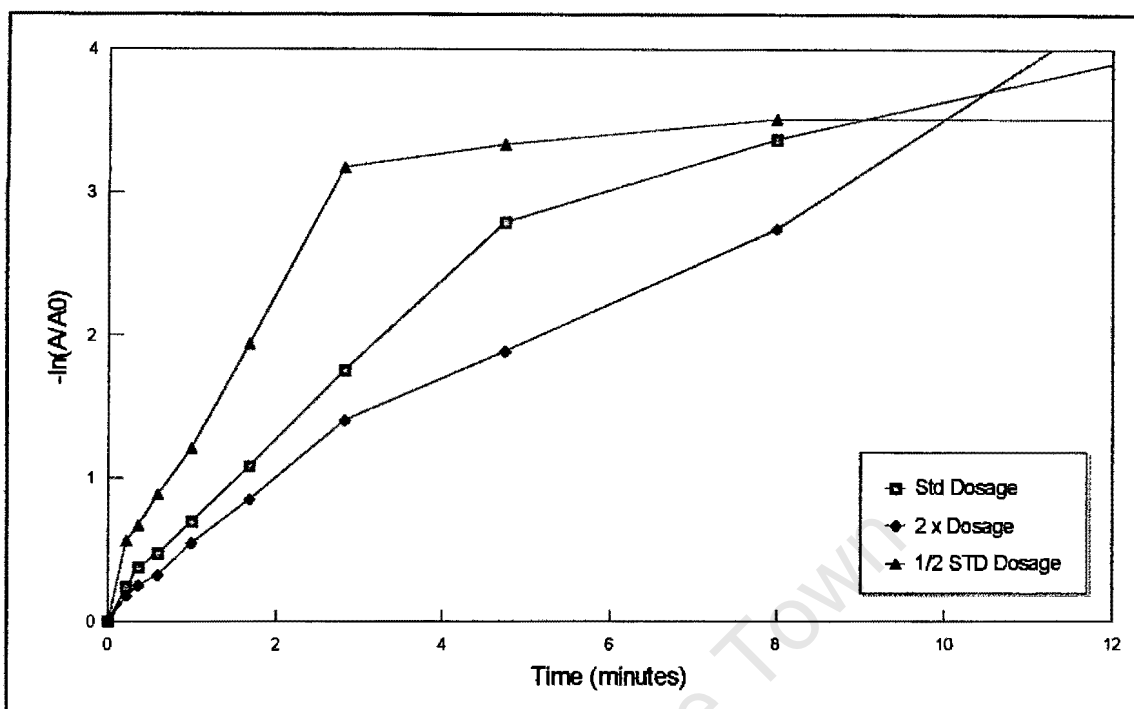


Figure 6.9 - Effect of Collector Dosage on PNBX Adsorption

Figure 6.10 shows the same information as Figure 6.8 for DiC3 DTC in the form of  $\ln[A/A_0]$  against time, for all three concentrations. The slopes of the lines give the first order rate constants for the three tests. Here the trends are reversed. The half-standard dosage has the highest first order reaction rate, while the high dosage has the lowest. This result would be unexpected if the system were still assumed to be diffusion controlling, since in a diffusion controlling environment, the double dosage would provide double the driving force and hence double the adsorption rate. In a diffusion controlled reaction, the rate constant would therefore be the same for all collector doses. These data simply confirm the fact that this system is no longer diffusion controlled. at the same time if the system were surface reaction controlled, increased collector dosage would be expected to provide no improvement in adsorption performance and hence the rate constant would be inversely proportionate to dosage. This is not the case (with first order rate constant for standard dosage = 0.569, while

the rate of  $2 \times \text{STD} = 0.401$  ), thus either the adsorption reaction is affected by both diffusion and surface reaction or another mechanism is acting on the system.



**Figure 6.10** - Effect of Collector Concentration on DiC3 Adsorption Rate Constant

In terms of how this might affect the conditioning of minerals there are two ways to look at the issue. Firstly, and possibly more appropriately for industry, the duration required to achieve optimum adsorption can be analyzed. From Figure 6.8 it can be seen that for the double dosage of  $5 \mu\text{moles/g}$ , the optimum level of approximately  $2.2 \mu\text{moles/g}$  DiC3 DTC collector uptake was reached within one minute of commencing conditioning. For the standard dosage, this level was only reached after 5 to 10 minutes of conditioning. On a minerals processing plant, this can be translated into the choice between using standard conditions or adding an extra 80 g/ton of collector to effect an 80 to 90 % savings in equipment, maintenance and power costs brought about by the reduced conditioning required. Stassen recommends an optimum conditioning power input of 10 kWh/ton. This might mean a ninety percent saving, translating to 9 kWh/ton energy saving. At a saving of 60 c to R 1,50 per ton on energy costs alone, it might well be cost effective to overdose with collector. The tests with PNBX show, though, that cognisance must always be taken of the collector's limit of solubility.

Secondly, there is once again a trade-off between two important variables. As dosage is increased, the first order rate constant is reduced. In this case, the increase in collector available for reaction more than off-sets the reduction in reaction rate. It may



be possible, however, to reach a situation where no advantage is gained by increasing the collector dosage.

What these data, and the previous section, help to highlight is the potential for optimisation of conditioning of mineral according to economic criteria (as well as the need to understand the opposing mechanisms affecting the conditioning efficiency). In a plant environment, where a proper factorial analysis of the variables of conditioning might be difficult, this optimisation is not usually carried out effectively.

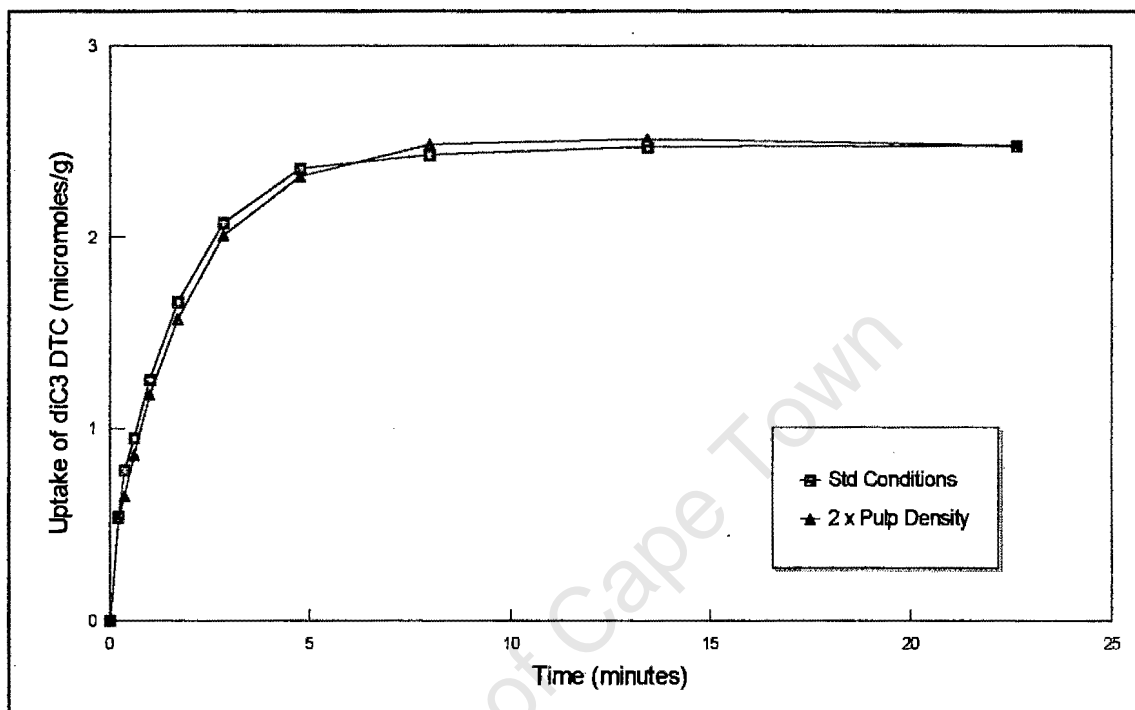
Several optimization methods and experimental design tools are available [Austin and Henwood, 1991] for use in optimising operating systems on-line. Evolutionary design tools such as EVOP (Evolutionary Operation) and SSDEVOP (Simplex Self Directing Evolutionary Operation) allow for a plant to gradually migrate to optimum operating conditions without drastic changes in the input or output variables. Since laboratory scale conditioning can be seen to be very different to that in a plant, these tools would provide the best means of reaching the most economically beneficial compromise between power, time and collector dosage.

## 6.9 Influence of Pulp Density

The work of Anderson [1988] showed that conditioning efficiency could be greatly enhanced through reduction in the pulp water content, or more precisely, increase in pulp density. In the present work, using the diC3 DTC-pyrite system, a similar experiment was carried out at standard conditions, except that the water content in the conditioning vessel was halved (run number 10D). Thus for the same collector dosage, not only was the power input per unit volume doubled (as in section 6.6 above), but the initial concentration of collector (defined as  $\mu\text{l/l}$  slurry) was also doubled. Since the adsorption of collector onto the pyrite was calculated to be first order in collector concentration (section 6.4), it was anticipated that the initial reaction rate would be doubled. While the advantage of increased power input was shown above to be negligible, increased collector concentration is expected to result in substantial increases in adsorption rates.

The results of the experiment are plotted in Figure 6.11 which shows the adsorption profiles for both standard pulp density and double pulp density. As may be seen, the curves overlap each other. This implies that adsorption rate was unaffected by the

increase in pulp density and conditioning power. It has already been shown that conditioning power input does not play a major role in improving collector uptake for this system (section 6.6). However, the lack of improvement as a result of increased concentration goes totally against all expectation. More specifically it contradicts the findings of section 6.8 above that adsorption rate is a function of collector concentration.



**Figure 6.11 - Effect of Pulp Density on diC3 DTC Collector Adsorption**

A dimensional analysis of the results obtained gives a hint as to the possible reaction mechanism resulting in this apparent anomaly. Three trials of importance were isolated:

- 1) Standard conditioning
- 2) Standard conditioning, but with double collector dosage.
- 3) Halved water content, but standard pyrite and collector dosage

The dependent variable is reaction rate, while the input variables are: volume and collector concentration.

Simply put, the rates achieved can be extracted from the input variables using the function:

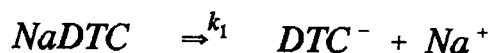
$$\text{Rate} = k \cdot \text{volume} \cdot \text{collector concentration}$$

This implies that the rate controlling reaction is a liquid volume rate reaction, dependent on both concentration and volume. Adsorption, on the other hand is a surface reaction, independent of volume but not independent of concentration.

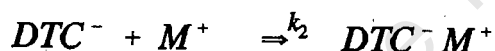
There are at least two possible reaction mechanisms which could give these results:

### 6.9.1. Slow Ionisation of the Collector

The mechanism hypothesised here is a two step reaction, involving the ionisation of molecular diC3 DTC, followed by the adsorption reaction onto the mineral surface. This could be represented as follows:



and



where

$k_1$  = rate constant for ionisation

$k_2$  = rate constant for adsorption

Therefore,

$$\text{Rate} = k_1[DTC] + k_2[DTC^-][M^+]$$

If  $k_2 \ll k_1$ , that is the rate is ionisation controlling, then,

$$\text{Rate of uptake} = k_1[DTC].\text{volume}$$

This proposed mechanism is able to explain the results of the three different situations isolated for analysis.

The strongest case against this mechanism is that ionisation is normally assumed to be instantaneous. Thus  $k_1 \approx 0$  and the mechanism no longer produces the results observed in the tests. This mechanism also implies that reaction rate is unaffected by mineral surface area, or availability of active sites. An effective negative test for this mechanism, then, is to determine the effect of halving mineral content of the slurry on collector uptake. Figure 6.12 shows the result of such a reduction in pyrite (run number 16D), with all else remaining at

standard conditions. The rate of adsorption per gram of pyrite can be seen to remain constant for both test levels of pyrite. For the overall system, this effectively halves the total rate of collector adsorption. Thus reaction kinetics are strongly affected by availability of the pyrite mineral. This hypothesis has, therefore, been disproved.

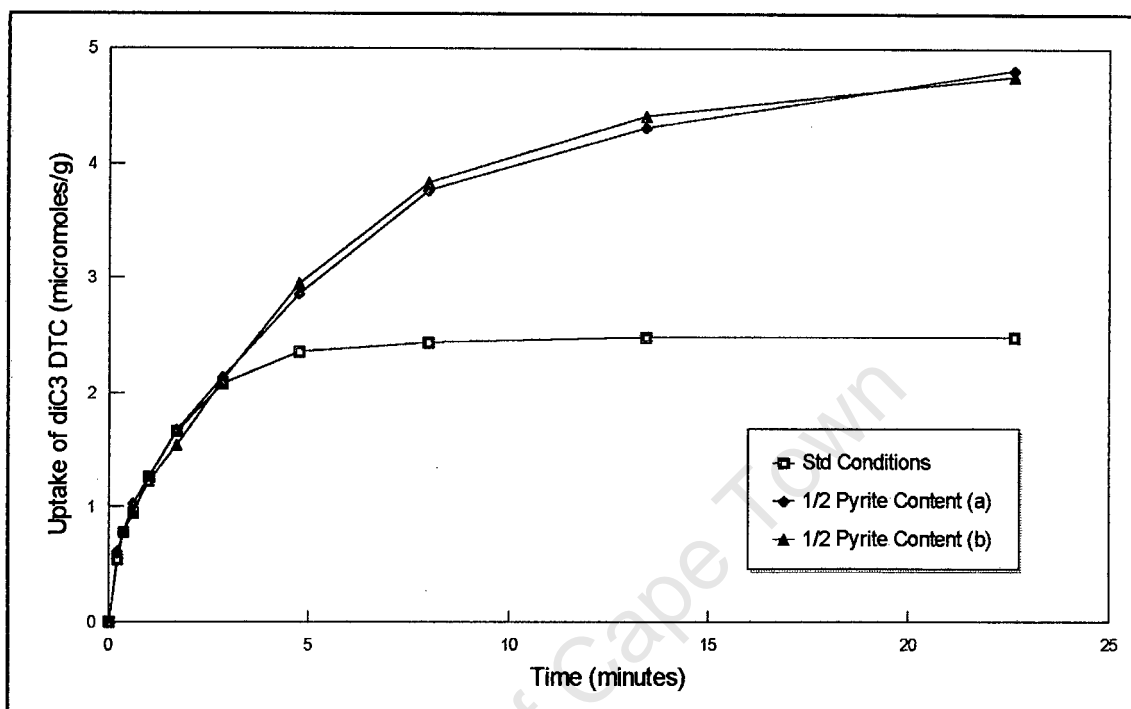
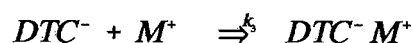
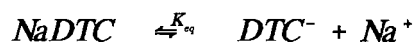


Figure 6.12 - Effect of Pyrite Content on diC3 DTC Collector Adsorption

### 6.9.2. Ionisation Constant of the Collector

The second proposed mechanism again involves two steps. This time an instantaneous ionisation of molecular diC3 DTC is assumed, but the extent of ionisation is limited. The second reaction of the collector adsorbing to the mineral surface remains as above. This is represented as follows, where  $K_{eq}$  = equilibrium constant of ionisation/dissociation:



Therefore,

$$\text{Rate} = k_3 [DTC^-] [M^+]$$

Or

$$\text{Rate} = k_3 [M^+] K_{eq} [\text{NaDTC}] / [\text{Na}^+]$$

For this case, the previous observation that the system is well mixed is used. It is assumed that diffusion to the mineral surface is much more rapid than the surface reaction.

Now, after a given fraction,  $x$ , of NaDTC has been adsorbed, we have  $(1-x)$  NaDTC remaining. If the equilibrium were almost entirely shifted to the molecular phase of NaDTC, we have in the case of standard conditioning:

$$K_{eq} = \frac{[\text{Na}^+] \cdot [\text{DTC}^-]}{[\text{NaDTC}]}$$

going to,

$$K_{eq} = \frac{x \cdot [\text{DTC}^-]}{1-x}$$

and hence,

$$[\text{DTC}^-] = K_{eq} \cdot \frac{1-x}{x}$$

For the case where water content is halved, the concentration of NaDTC in solution is doubled, but so is the removal of  $\text{DTC}^-$  and the buildup of Sodium ions in solution after equivalent extents of adsorption. This gives the following equilibrium equation:

$$K_{eq} = \frac{2x \cdot [\text{DTC}^-]}{2 \cdot (1-x)}$$

and hence,

$$[DTC^-] = K_{eq} \cdot \frac{1-x}{x}$$

Thus, the concentration of  $DTC^-$  is exactly the same for any level of collector adsorption. Since the rate is controlled by this ionised component of  $NaDTC$ , the rates must be the same for both cases. This is what was observed.

This process has been idealised by the assumption that the ionisation is strongly shifted to the molecular phase. But this is supported by the literature: dithiocarbamates are indeed found to be weakly ionised. For di-n-propyl dithiocarbamic acid, the  $pK_a \approx 5$  [Thorn and Ludwig, 1962]. From the mechanism shown in Figure 4.2 this represents the equilibrium between state II and state III. Thus in a solution of pH 4, the ionic form of the acid is only present in 1/10 of the concentration of the molecular form. This indicates that diC3 DTC is indeed weakly ionised and the mechanism described above is possible.

In the case where the liquid volume remains constant, but the concentration of collector has been doubled, the extent of removal from solution is  $x$ , as for the standard case. This gives:

$$K_{eq} = \frac{x \cdot [DTC^-]}{2-x}$$

and hence,

$$[DTC^-] = K_{eq} \cdot \frac{2-x}{x}$$

The initial rate of reaction is measured when  $x$  is small. For small  $x$ , the concentration of  $[DCT]$  is double that for standard conditions.

This mechanism also holds for the case covered in section 6.9.1 where mineral content is halved. Thus it appears that this proposed mechanism very adequately describes the observations made.

This proposed mechanism provides valuable insight into concentration or pulp density effects on partially dissociated collectors. This work shows that the degree to which dissociation can be achieved can strongly influence the rate of

adsorption of collector onto the mineral surface. Also shown is that, for well mixed systems, increasing pulp density need not be as advantageous as might be supposed. Especially where high pulp density causes mixing and transport problems, it may even be advantageous to dilute the slurry.

#### **6.10. Correlation between conditioning and flotation results**

From the preliminary work with both the quartz-amine system and the pyrite-thiol system, it was seen very clearly that a number of conditioning variables very strongly affect the adsorption of collector onto the mineral surface and also the flotation response of the mineral. However, this work also showed that in well mixed systems, adsorption was extremely rapid. This resulted in adsorption going to completion during flotation, in the case of the amine collector (section 4.5.2.3) HPYC.

The pyrite-thiol tests were the most successful in terms of being able to measure extent of adsorption onto the mineral surface. Since all of the tests shown in Figure 4.11 were conditioned for 25 minutes, it is known that adsorption reached completion. In this case adsorption correlated very closely to flotation response. The correlation, up to the optimum dosage, was approximately linear.

Adsorption was chosen as the measure for conditioning efficiency. Thus, for this case, it was found possible to correlate conditioning efficiency to flotation results. It is the author's belief that this correlation would extend to all of the variables tested using collector adsorption as a measure for conditioning efficiency. Unfortunately the rate of the continued reaction prevents a test of this hypothesis. A much larger system may provide the key to correlating collector adsorption to flotation results for all conditions.

Thus the final objective of this thesis, to relate conditioning effects to flotation, was only partially achievable. It is proven above that adsorption studies correlate to flotation results in all of the tests where conditioning during flotation was no longer significant. In all other cases, the conditioning during flotation made comparison meaningless. This is the problem that plagued Stassen as well. Further work using industrial-scale equipment should be performed to provide this correlation between flotation and conditioning efficiency measurements.

## 6.11. Limitations of this Work

As with much experimental work, this study includes a number of assumptions and simplifications. These limitations on the accuracy or portability of the study to full-scale should be understood. This will allow the experienced reader to know the limit of the applicability of this work to other areas of conditioning. The following are the major limitations of this work.

- (a) Well mixed system - Conditioning vessels of the dimension used are, by necessity, well mixed, since a high energy input is required to keep the mineral particles in suspension. Scale-up of a conditioning vessel usually centres around suspension of particles, but solid suspension in large tanks requires far less power input per unit volume. Scale-up using constant power input per unit volume is often difficult, since it requires very large motors, which are expensive and inefficient. Hence large conditioning tanks are usually poorly mixed.

The effect of this is that power input is far more important in large conditioning vessels than it was shown to be in this work, as evidenced by comparison with Stassen's work. This might also have an effect on the relative adsorption rates of various collectors, as diffusivity of the collectors may play larger role, than for the small well mixed system.

- (b) Low pulp density - The very low pulp density of 1%, necessary for these tests owing to the shortage of available pyrite, contrasts sharply with pulp densities of around 30% typically found in industry. The low pulp density reduces the interactive effects of solids, as well as resulting in different types of shear occurring. These interactive effects are most commonly seen as viscosity effects.

One mitigating factor in favour of this low pulp density, is that the pyrite content of the pulp is realistic when compared with that of typical pyrite slurries. The pyrite content of slurries is usually in the region of 0.5 to 5% of the solids content. Hence the pyrite content of these tests is consistent with industrial separations.



- (c) High pyrite grade - This system used almost pure pyrite, with the result that interference by gangue mineral played no part in the adsorption profiles achieved. While gangue mineral is believed not to adsorb collector, it does reduce the surface area available on only partially liberated pyrite particles. As mentioned above, gangue also adds particle-particle interaction forces to the already complex system.
- (d) Adsorption vs Floatability - The speed at which the adsorption reaction occurred precluded the possibility of measuring the floatability of any given extent of adsorption, unless the adsorption had reached completion. This is because the small scale of the test work resulted in a well mixed system. It was necessary to assume that a given extent of adsorption resulted in a fixed floatability, allowing comparison of effectiveness of conditioning by analysing the extent of adsorption.

This assumption need not be true, since collector can orientate differently on the mineral surface, depending on the conditions of adsorption. Most tests, however, were performed over a very limited range of conditions and hence the adsorption pattern is expected to be similar for similar extents of adsorption.

- (e) Oxygen is freely available - It was not possible in these tests to limit the availability of oxygen (though attempts were made to reduce oxygen to rate limiting levels by Bradshaw [1994]). In an industrial application, the liberation of mineral surface through crushing and grinding results in oxygen removal as a result of oxidation of the new surfaces. Hence, the system may be oxygen limiting. Most surface reactions of thiols cannot occur in the absence of oxygen, which catalyses the electron transfer to the pyrite surface. Therefore, in oxygen limiting systems, reaction rate can be severely retarded.

This work does not attempt to provide definitive answers to the problem of effective conditioning. Rather, it attempts to uncover a number of the areas in which conditioning plays an important role in altering the floatability of minerals. Thus the results have been interpreted to be generally applicable. It is the opinion of the author that these limitations do not negate the general usefulness of the results. This is especially true since most of the limitations above refer only to the relative dominance

of either diffusion or reaction control. Whereas, this work concentrates on the need to understand which mechanism controls, and to capitalise on this.

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## CHAPTER 7 - CONCLUSIONS

This work set out to answer a number of questions on conditioning, with the following steps to be undertaken to provide the answers:

- (1) Clearly define conditioning.
- (2) Determine a useful measure of conditioning efficiency.
- (3) Evaluate the effect of conditioning variables on efficiency.
- (4) Determine the effect of these variables in flotation by correlating conditioning and flotation results.

Of these stages only stage (4) could not be fully implemented. This was because the limitations of high intensity mixing imposed by laboratory scale flotation systems precluded any accurate correlation between conditioning and flotation. Below is a summary of the results from the work done for each of these stages.

Conditioning had been previously only loosely defined in the flotation literature, with its connotations varying from one minerals industry to another. This work identified two distinct aspects of conditioning, namely:

Primary Conditioning- the physical preparation of the surface of the particles. This includes comminution, oxidation, acid leaching and bacterial pretreatment.

Secondary Conditioning- the process whereby prepared particles are rendered hydrophobic or hydrophilic through mixing, control of the environment and contacting with reagents.

This covered stage (1) of the work and made it possible to isolate the area to be studied. This was defined as:

*The mixing of prepared particles with collector with the aim of achieving contact and successful attachment or adsorption of collector onto the desired mineral, thereby rendering the surface hydrophobic for flotation.*

Analysis of the literature on previous work on conditioning gave important insight into the problems of measuring conditioning effects - especially in the area of separating flotation results from conditioning results. The work of Stassen [1990] was especially useful, in that it attempted to answer many of the questions posed by this work. The tool finally chosen to measure conditioning efficiency was extent of adsorption. A pyrite-thiol system was chosen as the best practical system for test work, after unsuccessful attempt to use a quartz-amine system.

Thus stage (2) was successfully completed, paving the way for stage (3), where the effect of variables of conditioning on conditioning efficiency were to be studied. First, though the important variables needed to be identified. Literature on previous work and heterogeneous stirred tank reactor theory suggested that the conditioning variables should include (tested variables are given in *italics*):

ORE :	Mineral type and degree of liberation
	Grind size, affecting such features as s/v ratio
	<i>Pulp density</i>
COLLECTOR :	<i>Type, including solubility, polarity and molecule size</i>
	<i>Dosage</i>
	<i>Attachment mechanism</i>
SYSTEM :	pH
	<i>Time</i>
	<i>Mixing (power and turbulence)</i>
	<i>Method of agitation (turbulence distribution)</i>
	Temperature
	Ionic Strength

Microflotation was chosen as the best system to use for correlation of flotation effects to conditioning effects. This was for the dual reasons that the froth phase is eliminated in microflotation, reducing masking of effects, and the intensity of conditioning can be limited to that required for suspension of the particles, since bubbles are produced by the sintered glass filter. The fact that the microflotation cell uses very small mineral samples was considered a bonus, since sample availability was extremely limited. Microflotation was also used to test the calculated doses to be used for the adsorption tests and to find a 'good' collector dosage.

The results of the adsorption tests on the above conditioning variables, as discussed fully in the previous chapter, must be seen in the light of data available in literature and reaction theory to be best utilised. The exact values themselves are meaningless, in that every system in flotation is unique and no result can be directly applied to another situation, even in scaling.

The results did show that conditioning can be explained in terms of heterogenous stirred tank reactions. As a result, conditioning effects can be predicted provided enough is known about the reaction occurring. While the actual importance of each variable is specific to the application and conditions used, they are all explained in terms of the adsorption of collector onto the mineral surface. Hence, the relative importance of diffusion and of the reaction, in controlling adsorption rate, determines the variables to be considered when optimising conditioning. Understanding the reaction mechanisms taking place between collector and mineral is a vital tool in understanding the expected effects of changing variables of conditioning.

Also considered were the industrial implications of the effects of variables on conditioning in an attempt to determine the optimum parameters for each variable. What was found is that with all variables, there is a trade-off between improved conditioning and increased costs. Use of a costing function appears to be the best method of optimising conditioning in industrial applications.

Some mention should be made of the variables found to have consistently the greatest effect on conditioning results:

1) *Effect of Collector Type* - It was shown that different collectors adsorb onto the mineral surface at different rates. Also they may have different equilibrium levels of adsorption. How this affects collector choice depends on the kinetics of the system and the extent of conditioning provided.

2) *Effect of Duration and Power of Conditioning* - In the conditioning process, the duration and power input into conditioning, were found to be the most important mechanical variables affecting adsorption. Previous work [Stassen 1990] suggested that energy input was of primary importance. This work, however, shows both theoretically and experimentally that this is not the case. Rather, the manner in which the energy is added, either through duration or power, is more crucial and depends largely on whether the system is diffusion rate controlled or surface reaction rate controlled.

Industrially, there is a trade-off between volume requirements to provide conditioning time, power consumption for turbulence and the improvement in flotation results. The optimal energy input for a plant could be calculated using a costing function.

3) *Effect of Collector Dosage* - Collector concentration was consistently shown to affect conditioning and flotation to a great extent. In both the quartz-amine and the pyrite-thiol systems flotation was linearly affected by collector dosage up to the level of optimum adsorption, beyond which the benefits were reduced markedly. It was also noted that overdosing with collector, in the case of thiols, gave rapid gains in the speed at which optimum adsorption was achieved. This concept of a trade-off between dosage and time is important in the industrial environment, where once again cost is the deciding factor.

The final test work produced some results which were contrary to predictions from literature. The most significant contradictions were:

1) *Best flotation occurs at adsorption levels below or close to mono-layer coverage.* For the quartz-amine system, this was shown to be the case, but for pyrite-thiol systems, the optimum dosage was as much as 30 times that required for mono-layer adsorption. It was hypothesised that the collector tends to accumulate in multi-layers on more active sites, with a larger dosage being required to ensure a substantial coverage of the surface area.

2) *Adsorption of thiols onto pyrite is diffusion controlling.* For the test system used in this work it was shown that diffusion had only a very limited effect on the adsorption of the thiols onto the pyrite surface. The evidence pointed very strongly to an adsorption controlling mechanism. The tests analysing the time and power variables of conditioning showed that changes in turbulence and hence diffusion potential had almost no effect on adsorption, while time was seen to be very important, indicating that reaction rate rather than diffusion was limiting. The apparent contradiction with literature is possibly explained by the small scale of the test work done. Large-scale systems are typically poorly mixed and hence diffusion is not sufficiently aided by the system turbulence. These are therefore diffusion controlled. The small scale of this work meant that the system was very well mixed and diffusion requirements were reduced, to the extent that the surface reaction became the rate limiting step.

3) *Conditioning efficiency is a direct function of ENERGY input into the system.* This work refutes this postulate and shows that the two components of energy, time and power, each have different extents of influence on conditioning efficiency. The same energy can be added to the system as different combinations of time and power which yield vastly different results. Hence energy input is not a variable of conditioning, but its components, time and power, are. In Stassen's test system, changes in power were more critical to conditioning efficiency than were changes in time. In this work it was found that power changes had almost no influence on the collector adsorption, but that time was a very important variable affecting collector efficiency. This is because conditioning is a heterogeneous reaction, and as such, efficiency is affected by diffusion mechanisms or by surface reaction mechanisms to greater or lesser degrees depending on the system. Either mechanism may be controlling, in which case either turbulence or reaction time would be the important factor affecting adsorption and hence conditioning efficiency.

4) *Increased pulp density increases the efficiency of conditioning.* Increasing pulp density usually increases the driving force of the adsorption reactions and hence the rate of the reaction. In this work, while reaction rates were increased by increasing collector doses, increased pulp density yielded no change to the adsorption of dipropyl dithiocarbamate onto pyrite. This led to further investigation and the development of a reaction mechanism for diC3 DTC, which included a partial ionisation of molecular DiC3 DTC to the reactive ionic form, which very adequately explains the results seen. The conclusion here was that it is important to understand the reaction mechanisms of the collector. In this was predictions can be made as to the effect of a change in any variable.

This work answers some questions on conditioning, dispels some myths, restates old questions and raises many new questions about the subprocess of conditioning to be studied on the path to a clear understanding of the processes of flotation.

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## **APPENDIX A. - Derivation of Expression for R in Stassen's Equations**

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Stassen [1990] provides the following derivation for the term  $R$  in his equations (italics represent quotation from Stassen's thesis):

*Assume  $R$  is proportional to the extent to which the surfaces of mineral particles are coated with collector. This is in accordance with the findings of investigators who found that the recovery of valuable mineral during flotation is proportional to the amount of collector in the flotation concentrate, the surface area of the floated mineral particles or the extent to which the surfaces of mineral particles are coated with collector. Less than a complete monolayer of collector is sufficient for flotation with xanthates and many other collectors.*

Thus

$$R \propto \Psi_A$$

so that

$$R \propto \left[ 1 - e^{-k_c(P/V)_c^\gamma t_c - k_f(P/V)_f^\gamma t_f} \right]$$

Further if  $R \rightarrow R^{\min}$  as  $t_c \rightarrow 0$  and  $R \rightarrow R^{\max}$  as  $t_c \rightarrow \infty$ , then

$$(R^{\max} - R) / (R^{\max} - R^{\min}) = e^{-k_c(P/V)_c^\gamma t_c}$$

or

$$\ln [(R^{\max} - R) / (R^{\max} - R^{\min})] = -k_c(P/V)_c^\gamma t_c$$

which is of the same form as the expression developed for the Klimpel flotation rate constant,  $k$ .

## **APPENDIX B. - Stassen's Experimental Data**

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The following data were obtained by Stassen [1990] and used in his thesis to calculate the regression coefficients in his model. These data are taken directly from Appendix A4 of Stassen's thesis. The present thesis re-analyzes these data to determine if any additional information may be obtained from them. The results of this re-analysis can be found in Chapter 3.

No.	D/Dt	N	tc	P	E	Au		U3O8		S	
		(RPM)	(min)	(W)	kWh/t	R	k	R	k	R	k
A.1	0.33	800	18	42.1	1.26	94.12	7.21	41.32	2.42	91.93	4.91
A.2	0.33	900	18	60	1.8	95.06	7.8	43.33	2.72	93.78	5.02
A.3	0.33	1000	18	82.3	2.47	95.34	9.87	43.8	2.86	95.75	7.06
A.4	0.33	1100	18	109.5	3.28	96.04	7.83	45.16	2.85	95.19	6.94
A.5	0.33	700	18	28.2	0.85	94.04	6.01	42.39	2.27	91.29	3.82
A.6	0.33	600	18	117.8	0.53	95.02	4.58	41.51	1.71	92.13	2.4
A.7	0.25	1000	18	19.5	0.59	94.68	5.02	40.86	1.8	94.3	2.24
A.8	0.25	1100	18	26	0.78	96.83	3.75	42.78	1.59	95.34	2.32
A.9	0.25	900	18	14.2	0.43	94.01	4	40.89	1.5	93.54	1.95
A.10	0.25	800	18	10	0.3	94.75	4.69	39.17	1.56	91.35	1.7
A.11	0.25	700	18	6.7	0.2	95.78	3.41	41.43	1.05	94.78	1.18
A.12	0.4	500	18	25.6	0.77	94.98	5.29	36.85	1.51	92.85	2.85
A.13	0.4	700	18	70.2	2.11	95.13	7.42	42.93	2.55	95.49	5.52
A.14	0.4	800	18	104.8	3.14	96.52	6.47	46.45	2.57	96.04	6.22
A.15	0.4	900	18	149.2	4.48	95.19	9.24	46.14	3.54	95.29	8.92
A.16	0.4	1000	18	204.7	6.14	96.67	10.36	45.84	3.14	96	9.38
A.17	0.4	1100	18	272.4	8.17	98.64	5.8	47.23	2.67	97.67	6.68
A.18	0.5	1100	18	831.4	24.94	98.06	7.31	48.22	3.09	98.31	7.22
A.19	0.5	1000	18	624.6	18.74	97.23	11.08	46.8	3.3	97.34	9.38
A.20	0.5	900	18	455.4	13.66	97.15	10.15	47.75	3.33	96.52	9.03
A.21	0.5	800	18	319.8	9.59	96.62	10.19	45.99	3.24	93.98	7.61
A.22	0.5	700	18	214.3	6.43	95.59	10.1	45.95	3.05	93.87	7.48
A.23	0.5	600	18	134.9	4.05	94.99	7.97	44.26	2.97	93.57	6.07
A.24	0.5	500	18	78.1	2.34	95.03	7.46	42.46	2.82	89.76	4.95
A.25	0.5	500	36	78.1	4.68	96.17	5.65	46.27	2.53	94.8	4.96
A.26	0.5	500	9	78.1	1.17	94.48	7.76	41.58	2.29	90.06	3.67
A.27	0.5	500	72	78.1	9.37	95.59	7.12	43.85	2.53	95.11	7.27
A.28	0.5	500	4.5	78.1	0.59	94.15	5.71	41.36	2.23	87.52	1.95
A.29	0.5	700	9	214.3	3.21	95.12	8.22	43.8	2.82	97.95	4.96
A.30	0.5	700	72	214.3	25.71	97.74	9.83	48.58	2.9	97.5	10.42
A.31	0.5	700	4.5	214.3	1.61	95.46	8.73	42.16	2.68	94.17	3.53
A.32	0.5	700	36	214.3	12.86	97.03	7.54	47.22	2.8	97.33	7.72
A.33	0.5	900	9	455.4	6.83	97.1	12.42	46.59	3.37	95.91	7.95
A.34	0.5	900	72	455.4	54.64	98.61	6.09	48.4	2.09	98.2	7.34
A.35	0.5	900	4.5	455.4	3.42	94.91	9.15	41.88	2.82	92.98	3.24

No.	D/Dt	N	t <sub>c</sub>	P	E	Au		U3O8		S	
		(RPM)	(min)	(W)	kWh/t	R	k	R	k	R	k
A.36	0.5	900	36	455.4	27.32	98.18	6.8	47.8	2.83	97.78	8.32
A.37	0.5	1100	9	831.4	12.47	97.49	9.79	46.23	3.32	97.09	9.12
A.38	0.5	1100	36	831.4	49.88	97.26	9.3	48.54	2.82	98.16	10.64
A.39	0.5	1100	4.5	831.4	6.24	96.67	8.91	45.03	2.93	97.79	6.19
A.40	0.5	1100	72	831.4	99.77	97.3	5.03	46.2	1.92	96.56	7.01
A.41	0.33	400	18	5.3	0.16	92.11	4.27	36.2	0.96	92.72	1.2
A.42	0.4	400	18	13.1	0.39	93.47	4.75	41.17	1.75	93.15	2.18
A.43	0.4	300	18	5.5	0.17	92.89	4.45	39.86	1.49	94.14	1.35
A.44	0.5	300	18	16.9	0.51	93.3	4.44	39.92	1.87	91.05	1.88
A.45	0.5	400	18	40	1.2	93.47	7.09	41.27	2.68	91.87	3.6
A.46	0.4	1100	9	272.4	4.09	96.25	10.5	46.39	3.3	95.99	8.44
A.47	0.4	300	72	5.5	0.66	94.03	2.69	41.23	1.08	92.31	1.98
A.48	0.33	300	72	2.2	0.27	93.8	2.55	38.46	0.73	94.45	1.44
A.49	0.4	1100	4.5	272.4	2.04	94.3	6.96	41.02	2.53	93.66	4.04
A.50	0.4	1100	72	272.4	32.69	97.21	7.87	49.16	2.67	97.48	10.01
A.51	0.4	1100	36	272.4	16.35	96.79	7.44	43.85	2.35	97.41	7.85
A.52	0.4	900	72	149.2	17.91	97.29	7.02	45.47	2.93	97.38	7.36
A.53	0.4	900	4.5	149.2	1.12	95.75	7.01	43.44	2.47	94.34	3.13
A.54	0.4	900	36	149.2	8.95	96.34	10.66	44.99	3.22	96.94	9.57
A.55	0.4	900	9	149.2	2.24	94.97	7.34	41.6	2.56	93.73	4.32
A.56	0.4	700	72	70.2	8.42	96.6	6.47	45.08	2.37	96.39	6.38
A.57	0.4	700	4.5	70.2	0.53	93.5	5.24	40.72	1.97	93.61	1.67
A.58	0.4	500	72	25.6	3.07	95.3	5.31	44.62	2.11	95.13	4.9
A.59	0.4	500	9	25.6	0.38	93.82	5.16	39.47	2.09	91.4	1.68
A.60	0.4	500	4.5	25.6	0.19	94.72	4.39	40.59	1.66	92.56	0.92
A.61	0.4	500	36	25.6	1.54	94.51	5.06	40.19	1.78	93.51	3.38
A.62	0.4	700	36	70.2	4.21	97.05	6.25	45.26	2.36	95.4	5.88
A.63	0.4	700	9	70.2	1.05	96.64	4.98	39.89	2.21	91.18	2.57
A.64	0.4	700	9	70.2	1.05	94.98	6.95	42.87	2.73	92.78	3.89
A.65	0.4	600	18	44.2	1.33	94	7.16	42.4	2.4	93.28	3.84
A.66	0.4	500	18	25.6	0.77	94.13	6.43	42.09	2.32	91.85	2.89
A.67	0.5	500	18	78.1	2.34	95.21	8.9	43.11	2.94	94.69	5
A.68	0.5	700	4.5	214.3	1.61	94.86	7.52	42.25	2.51	93.72	2.97
A.69	0.5	900	4.5	455.4	3.42	96.65	9.7	43.42	3.15	95.93	5.2
A.70	0.33	500	18	10.3	0.31	92.85	5.08	38.75	1.56	90.53	2.25
A.71	0.5	300	72	16.9	2.02	96.73	4.85	41.4	1.87	94.74	3.82
A.72	0.5	300	36	16.9	1.01	93.45	5.43	40.42	1.92	90.98	2.92
A.73	0.25	700	18	6.7	0.2	93.83	4.5	40.42	1.76	92.78	1.48
A.74	0.4	1100	36	272.4	16.35	97.22	11.01	44.3	3.06	97.51	10.65

## **APPENDIX C. - Surface Area Calculations**

University of Cape Town

Calculations of particle surface areas was necessary to determine the collector dosage required for mono-layer coverage of the quartz and pyrite minerals used. Particle surface area was calculated for cubic and for spherical particles. Below are the derivations of formulae for surface area per gram of particles for cubic and spherical particles:

## CALCULATIONS FOR CUBIC PARTICLES

$$\text{Total surface area (TS)} = \sum \text{all particle surfaces}$$

$$\text{TS/gram particles} = (\text{no. particles/gram}) \times (\text{surface area of each particle})$$

$$\text{surface area of each particle} = 6 \times H \times H$$

$$\text{no. particles/gram} = 1/(\text{mass of each particle})$$

$$\text{mass of each particle} = \text{density} \times \text{volume} = \rho \times H \times H \times H$$

$$\text{no. particles/gram} = 1/(\rho \times H \times H \times H)$$

$$\text{TS/gram} = (1/(\rho \times H \times H \times H)) \times (6 \times H \times H)$$

$$\underline{\text{TS/gram}} = \underline{6/(\rho \times H)}$$

## CALCULATIONS FOR SPHERICAL PARTICLES

The same logic as above applies except that:

$$\text{surface area of each particle} = 4 \Pi (\text{Diameter}/2)^2$$

$$\text{volume of each particle} = 4/3 \Pi (D/2)^3$$

Therefore,

$$\text{TS/gram} = (1/(\text{density} \times 4/3 \Pi (D/2)^3)) \times (4 \Pi (D/2)^2)$$

$$\underline{\text{TS/gram}} = \underline{6/(\rho \times D)}$$

## **APPENDIX D. - Quartz-Amine Microflotation Test Data**

University of Cape Town

# APPENDICES

Run No.	Sample	Paper	Gross	Net	Paper	Gross	Net	Corr. Frae	Liquid	Collector	Condition	Impeller	Air Flow	Particle	Filtration
	Mass	Weight	Recovery	Recovery	Loss	Loss	Loss	Recovered	Volume (ml)	Dozege(ml)	Time (min)	Speed (rpm)	Rate (l/min)	Size (microns)	Time (min)

Comments

A1	7.5	0.9	5.88	4.98	0.9	1.16	0.260	0.688	150	3	2	500	constant	+75-106	2
A2	7.5	0.9	4.87	3.97	0.91	1.91	1.000	0.611	150	3	2	500	constant	+75-106	1
A3	7.5	0.91	7.21	6.3	0.92	1.07	0.150	0.857	150	6	2	500	constant	+75-106	1
A4	7.5	0.94	2.71	1.77	0.87	0.91	0.040	0.227	150	1.5	2	500	constant	+75-106	1
A5	7.5	0.94	6.14	5.2	0.94	0.98	0.040	0.697	150	3	0.5	500	constant	+75-106	1
A6	7.5	0.91	5.35	4.44	0.94	1.01	0.070	0.598	150	3	2	500	constant	+75-106	1
A7	7.5	0.94	5.86	4.92	0.91	1.03	0.120	0.667	150	3	2	500	constant	+35-53	1
A8	7.5	0.94	6.41	5.47	0.9	0.92	0.020	0.731	150	3	2	500	constant	+106	1

B1	7.5	1.027	6.629	5.602	1.033	1.166	0.131	0.760	150	3	2	500	constant	+75-106	1
B2	7.5	0.917	6.248	5.311	0.989	1.152	0.163	0.727	150	3	2	500	constant	+75-106	1
B3	7.5	0.959	5.523	4.564	0.996	1.058	0.060	0.613	150	3	2	500	constant	+75-106	1
B4	7.5	1.032	5.606	4.574	0.964	1.127	0.163	0.623	150	3	2	500	constant	+75-106	1
B5	7.5	1.026	5.807	4.881	1.007	1.074	0.067	0.657	150	3	2	500	constant	+75-106	1
B6	7.5	0.932	6.548	5.596	0.997	1.083	0.086	0.735	150	3	2	500	constant	+75-106	1
B7	7.5	0.935	5.55	4.615	0.97	1.1	0.130	0.626	150	3	2	500	constant	+75-106	1
B8	7.5	0.97	6.01	5.04	0.99	1.08	0.090	0.680	150	3	2	500	constant	+75-106	1
B9	7.5	0.98	6.57	5.59	0.95	1.03	0.080	0.753	150	3	2	500	constant	+75-106	1
B10	7.5	0.97	5.74	4.77	0.98	1.07	0.090	0.644	150	3	2	500	constant	+75-106	1
B11	7.5	1	5.91	4.91	1.01	1.1	0.090	0.663	150	3	2	500	constant	+75-106	1
B12	7.5	0.92	5.84	4.92	1.01	1.09	0.080	0.663	150	3	2	500	constant	+75-106	1
B13	7.5	0.96	5.65	4.69	1.01	1.08	0.070	0.631	150	3	2	500	constant	+75-106	1
B14	7.5	0.95	5.51	4.56	0.96	1.03	0.070	0.614	150	3	2	500	constant	+75-106	1
B15	7.5	0.91	5.31	4.4	0.98	1.03	0.050	0.591	150	3	2	500	constant	+75-106	1
B16	7.5	0.91	6.05	5.14	0.92	0.98	0.060	0.691	150	3	2	500	constant	+75-106	1
B17	7.5	0.97	4.98	4.01	0.99	1	0.010	0.535	150	2	2	500	constant	+75-106	1
B18	7.5	0.94	4.32	3.38	0.92	1.06	0.140	0.459	150	2	2	500	constant	+75-106	1
B19	7.5	0.94	4.35	3.41	1.03	1.16	0.130	0.463	150	2	2	500	constant	+75-106	1
B20	7.5	0.95	4.41	3.46	0.98	1.12	0.140	0.470	150	2	2	500	constant	+75-106	1
B21	7.5	0.97	4.01	3.04	1.02	1.1	0.080	0.410	150	2	2	500	constant	+75-106	1
B22	7.5	0.92	4.2	3.28	0.95	1.13	0.200	0.449	150	2	2	500	constant	+75-106	1
B23	7.5	1	4.53	3.53	0.99	1.13	0.140	0.480	150	2	2	500	constant	+75-106	1
B24	7.5	0.96	4.2	3.24	0.95	1.13	0.180	0.443	150	2	2	500	constant	+75-106	1
B25	7.5	0.94	5.03	4.09	0.98	1.28	0.300	0.568	150	2	2	500	constant	+75-106	1
B26	7.5	1	6.78	5.78	1	1.27	0.270	0.799	150	2	2	500	constant	+35-53	1
B27	7.5	0.96	6.73	5.77	0.95	1.23	0.280	0.788	150	2	2	500	constant	+35-53	1
B28	7.5	0.99	6.8	5.81	1.03	1.16	0.130	0.788	150	2	2	500	constant	+35-53	1
B29	7.5	0.97	3.58	2.61	0.96	1.01	0.050	0.350	150	2	2	500	constant	+106	1
B30	7.5	0.91	2.76	1.85	0.89	0.97	0.080	0.249	150	2	2	500	constant	+106	1

Mixed up new evolution of HPYC

Installed flow meter to improve consistency

Floated for 15 sec too long

Filtration start was delayed

New setup - 2nd HPYC  
Smaller Container

APPENDICES

Run No.	Sample	Paper	Gross	Nett	Paper	Gross	Nett	Corr. Fnc	Liquid	Collector	Condition	Impeller	Air Flow	Particle	Filtration
	Mass	Weight	Recovery	Recovery	Loss	Loss	Loss	Recovered	Volume (ml)	Dosage(ml)	Time (min)	Speed (rpm)	Rate (l/min)	Size (micron)	Time (min)

Comments

C1	10	0.64	2.39	1.75	0.66	0.69	0.030	0.176	200	3	2	900	0.18	+75-106	2
C2	10	0.63	2.58	1.95	0.63	0.65	0.020	0.195	200	3	2	500	0.18	+75-106	2
C3	10	0.67	4.55	3.88	0.63	0.65	0.020	0.389	200	5	2	500	0.18	+75-106	2
C4	10	0.65	4.22	3.57	0.68	0.73	0.030	0.359	200	5	2	1000	0.18	+75-106	2
C5	10	0.68	5.36	4.68	0.63	0.66	0.030	0.469	200	5	0.5	1000	0.18	+75-106	2
C6	10	0.68	4.56	3.88	0.78	0.8	0.020	0.389	200	5	0.5	2000	0.18	+75-106	2
C7	10	0.63	3.96	3.33	0.63	0.68	0.030	0.355	200	5	0.5	500	0.18	+75-106	2
C8	10	0.7	3.47	2.77	0.67	0.7	0.030	0.278	200	5	8	500	0.18	+75-106	2
C9	10	0.62	3.85	3.23	0.63	0.65	0.020	0.324	200	5	2	500	0.18	+75-106	2
C10	10	0.68	4.24	3.56	0.69	0.72	0.030	0.357	200	5	2	500	0.18	+75-106	2
C11	10	0.65	4.25	3.6	0.68	0.68	0.000	0.360	200	5	2	500	0.18	+75-106	2
C12	10	0.68	4.55	3.87	0.64	0.63	-0.010	0.387	200	5	2	500	0.18	+75-106	2
C13	10	0.68	5.05	4.37	0.63	0.64	0.010	0.437	200	5	2	500	0.18	+75-106	2
C14	10	0.67	4.54	3.87	0.66	0.66	0.000	0.387	200	5	2	500	0.18	+75-106	2
C15	10	0.61	4.61	4	0.67	0.69	0.020	0.401	200	5	2	500	0.18	+75-106	2
C16	10	0.64	6.46	5.82	0.64	0.65	0.010	0.583	200	5	2	500	0.18	+75-106	2
C17	10	0.69	6.51	5.82	0.65	0.65	0.000	0.582	200	5	2	500	0.18	+75-106	2
C18	10	0.63	5.98	5.35	0.65	0.66	0.010	0.536	200	5	2	500	0.18	+75-106	2
C19	10	0.65	5.81	5.16	0.68	0.7	0.020	0.517	200	5	2	500	0.18	+75-106	2
C20	10	0.61	5.6	4.99			0.000	0.499	200	5	2	500	0.18	+75-106	2
C21	10	0.65	5.08	4.43			0.000	0.443	200	5	2	500	0.18	+75-106	2

Fixed air leak

D1	10	0.64	5.69	5.05			0.000	0.505	200	5	2	500	0.18	+75-106	2
D2	10	0.68	5.63	4.95			0.000	0.495	200	5	2	500	0.18	+75-106	2
D3	10	0.63	5.75	5.12			0.000	0.512	200	5	2	500	0.18	+75-106	2
D4	10	0.66	5.78	5.12			0.000	0.512	200	5	2	500	0.18	+75-106	2
D5	10	0.62	5.84	5.22			0.000	0.522	200	5	2	500	0.18	+75-106	2
D6	10	0.67	6.72	6.05	0.64	0.64	0.000	0.605	200	5	0.7	500	0.18	+75-106	2
D7	10	0.68	5.74	5.06	0.6	0.61	0.010	0.507	200	5	5.65	500	0.18	+75-106	2
D8	10	0.62	5.98	5.36	0.64	0.64	0.000	0.536	200	5	0.25	500	0.18	+75-106	2
D9	10	0.63	5.16	4.53			0.000	0.453	200	5	2	500	0.18	+75-106	2
D10	10	0.59	5.94	5.35	0.64	0.64	0.000	0.535	200	5	2	500	0.18	+75-106	2
D11	10	0.64	6.91	6.27	0.65	0.65	0.000	0.627	200	5	2	500	0.18	+75-106	2
D12	10	0.6	7.08	6.48	0.63	0.63	0.000	0.648	200	5	2	500	0.18	+75-106	2

Refrigerated HPTC - time is 11:40 am (Tues)

time 12pm

time 3:15 pm

time 4pm

Wed, 9 am

8:30 am Thurs

9 am Thurs

# APPENDICES

Run No.	Sample	Paper	Gross	Net	Paper	Gross	Net	Corr. Fac	Liquid	Collector	Conditioning	Impeller	Air Flow	Particle	Floatation
	Mass	Weight	Recovery	Recovery	Loss	Loss	Loss	Recovered	Volume (ml)	Dosage (ml)	Time (min)	Speed (rpm)	Rate (l/min)	Size (micron)	Time (min)
E1	10	0.64	8.08	7.44	0.66	0.69	0.030	0.746	200	2	2	500	0.04	+75-106	1
E2	10	0.62	7.11	6.49			0.000	0.649	200	2	0	500	0.04	+75-106	1
E3	10	0.61	4.17	3.56			0.000	0.356	200	1	2	500	0.04	+75-106	1
E4	10	0.62	4.82	4.2			0.000	0.420	200	1	2	500	0.04	+75-106	1
E5	10	0.57	4.18	3.61			0.000	0.361	200	1	2	500	0.04	+75-106	1
E6	10	0.64	4.93	4.29			0.000	0.429	200	1	2	500	0.04	+75-106	1
E7	10	0.6	4.86	4.26			0.000	0.429	200	1	2	500	0.04	+75-106	1
E8	10	0.63	4.76	4.13			-5.170	0.272	200	1	2	500	0.04	+75-106	1
E9	10	0.63	4.96	4.33			0.030	0.434	200	1	2	500	0.04	+75-106	1
E10	10	0.6	4.97	4.37			0.000	0.437	200	1	0	500	0.04	+75-106	1
E11	10	0.61	4.96	4.35			0.030	0.436	200	1	2	500	0.04	+75-106	1
E12	10	0.62	4.62	4			-0.020	0.399	200	1	0	500	0.04	+75-106	1
E13	10	0.64	4.97	4.33			-0.010	0.433	200	1	0	500	0.04	+75-106	1
E14	10	0.61	1.1	0.49			0.000	0.049	200	0	2	500	0.04	+75-106	1
E15	10	0.62	1.57	0.95			0.000	0.095	200	0.2	0	500	0.04	+75-106	1
E16	10	0.63	1.42	0.79			0.000	0.079	200	0.2	2	500	0.04	+75-106	1
E17	10	0.65	1.74	1.09			0.000	0.109	200	0.2	30	500	0.04	+75-106	1
E18	10	0.63	5.22	4.59			0.000	0.459	200	1	30	500	0.04	+75-106	1
E19	10	0.59	5.89	5.3			0.040	0.532	200	1	30	500	0.04	+75-106	1
E20	10	0.59	5.22	4.63			0.010	0.463	200	1	0	500	0.04	+75-106	1
E21	10	0.62	5.19	4.57			0.000	0.457	200	1	0	500	0.04	+75-106	1
E22	10	0.63	5.11	4.48			0.030	0.449	200	1	30	500	0.04	+75-106	1

Comments

Using new cone and stirring magnet

as above but small stirring magnet  
large stirrer but began ahead of time  
as above but small stirrer

12sec too much float



## **APPENDIX E. - Pyrite-Thiol Microflotation Test Data**

University of Cape Town

APPENDICES

Run No.	Sample	Paper	Gross	Net	Paper	Gross	Net	Fraction	Liquid	Collector	Conditioning	Impeller	Air Flow	Particle	Reaction
	Mass	Weight	Recovery	Recovery	Tailings	Tailings	Tailings	Recovered	Volume (ml)	Dosage(ml)	Time (min)	Speed (rpm)	Rate (l/min)	Size (micron)	Time (min)

Comments

F1	4	0.63	0.94	0.31	0.63	4.26	3.630	0.078	400	0	0	500	0.04	+75-106	1
F2	4	0.64	2.42	1.78	0.65	2.67	2.020	0.445	400	0	25	500	0.04	+75-106	1
F3	4	0.61	2.51	1.9	0.63	2.61	1.980	0.475	400	0	25	500	0.04	+75-106	1
F4	4	0.66	2.06	1.4	0.61	3.05	2.440	0.350	400	1.44	25	500	0.04	+75-106	1
F5	4	0.63	2.23	1.6	0.7	2.95	2.250	0.400	400	2.88	25	500	0.04	+75-106	1
F6	4	0.7	2.71	2.01	0.61	2.44	1.830	0.503	400	0.72	25	500	0.04	+75-106	1
F7	4	0.65	2.38	1.73	0.65	2.73	2.080	0.433	400	0	25	500	0.04	+75-106	1
F8	4	0.59	3.76	3.17	0.65	1.29	0.640	0.793	400	14.4	25	500	0.04	+75-106	1
F9	4	0.69	3.19	2.5	0.59	1.95	1.360	0.625	400	7.2	25	500	0.04	+75-106	1
F10	4	0.58	3.79	3.21	0.69	1.28	0.590	0.803	400	28.8	25	500	0.04	+75-106	1

Pyrite at pH 7 no conditioning  
15min conditioning at pH 4 with buffer

Repeat of 2

Reproducibility

## **APPENDIX F. - Pyrite-Thiol Adsorption Test Data**

University of Cape Town

The adsorption tests were numbered according to whether they were performed using PNBX or DTC, with the suffix P and D used respectively. Much of this work was performed in collaboration with D.J. Bradshaw, whose assistance is gratefully acknowledged.

TIME (minutes)	Run 1P PNBX STD Cond	Collector Adsorption (mols E-6)
0	0.392	0
0.13	0.351	0.26
0.67	0.287	0.67
1	0.245	0.94
2.82	0.137	1.63
8	0.007	2.46
22.63	0.005	2.47

Sample	TIME (minutes)	Run 2P PNBX STD Cond	Collector Adsorption (mols E-6)	Run 3P PNBX STD Cond	Collector Adsorption (mols E-6)	Run 4P PNBX Dos 1/4std	Collector Adsorption (mols E-6)	Run 5P PNBX Dos 10s	Collector Adsorption (mols E-6)	Run 6P PNBX 1000rpm	Collector Adsorption (mols E-6)
0	0	0.392	0	0.392	0	0.107	0	3.1	0	0.392	0.000
1	0.21	0.367	0.16	0.343	0.31	0.074	0.19	2.892	1.68	0.317	0.478
2	0.36	0.317	0.48	0.326	0.42	0.062	0.26	2.876	1.81	0.293	0.631
3	0.59	0.294	0.63	0.301	0.58	0.055	0.3	2.868	1.87	0.266	0.804
4	1	0.257	0.86	0.276	0.74	0.039	0.4	2.861	1.93	0.225	1.065
5	1.68	0.206	1.19	0.225	1.07	0.022	0.5	2.85	2.02	0.181	1.346
6	2.83	0.134	1.65	0.17	1.42	0.01	0.57	2.82	2.26	0.119	1.741
7	4.75	0.061	2.11	0.087	1.95	0.007	0.58	2.779	2.59	0.058	2.130
8	8	0.021	2.37	0.019	2.38	0.007	0.58	2.718	3.08	0.019	2.379
9	13.45	0.01	2.44	0.009	2.44	0.009	0.57	2.619	3.88	0.01	2.436
10	22.63	0.01	2.44	0.008	2.45	0.01	0.57	2.461	5.15	0.013	2.417
	30							2.369	5.9		
	38							2.315	6.33		

Sample No.	TIME (minutes)	Run 1D dic3 DTC STD Cond	Collector Adsorption (mols E-6)	Run 2D dic3 DTC 1000rpm	Collector Adsorption (mols E-6)	Run 3D dic3 DTC 390rpm	Collector Adsorption (mols E-6)	Run 4D dic3 DTC 1/2 of all	Collector Adsorption (mols E-6)	Run 5D OC6 DTC STD Cond	Collector Adsorption (mols E-6)
0	0.00	0.360	0.000	0.360	0.000	0.360	0.000	0.360	0.000	0.225	0.000
1	0.21	0.295	0.580	0.278	0.732	0.305	0.491	0.315	0.481	0.164	0.680
2	0.36	0.266	0.839	0.265	0.848	0.267	0.830	0.298	0.662	0.154	0.790
3	0.59	0.252	0.964	0.242	1.054	0.263	0.866	0.267	0.994	0.135	1.000
4	1.00	0.222	1.232	0.204	1.393	0.213	1.313	0.241	1.271	0.121	1.160
5	1.68	0.173	1.670	0.157	1.813	0.166	1.732	0.195	1.763	0.093	1.470
6	2.83	0.132	2.036	0.115	2.188	0.150	1.875	0.163	2.105	0.064	1.790
7	4.75	0.097	2.348	0.083	2.473	0.118	2.161	0.144	2.308	0.048	1.970
8	8.00	0.092	2.393	0.079	2.509	0.078	2.518	0.132	2.436	0.046	1.990
9	13.45	0.081	2.491	0.080	2.500	0.074	2.554	0.128	2.479	0.047	1.980
10	22.63	0.082	2.482	0.073	2.563	0.083	2.473	0.126	2.500	0.044	2.010

Sample No.	TIME (minutes)	Run 6D dic3 DTC 2* Dos	Collector Adsorption (mols E-6)	Run 7D dic3 DTC no ore	Collector Adsorption (mols E-6)	Run 8D dic3 DTC 707RPM	Collector Adsorption (mols E-6)	Run 9D dic3 DTC STD Cond	Collector Adsorption (mols E-6)	Run 10D dic3 DTC 1/2 H2O	Collector Adsorption (mols E-6)
0	0.00	0.630	0.000			0.360	0.000	0.360	0.000	0.630	0.000
1	0.21	0.548	0.820	0.321	0.685	0.286	0.685	0.299	0.545	0.523	0.535
2	0.36	0.520	1.100	0.323	0.833	0.270	0.833	0.283	0.688	0.500	0.650
3	0.59	0.495	1.350	0.328	1.037	0.248	1.037	0.263	0.866	0.458	0.860
4	1.00	0.422	2.080	0.343	1.343	0.215	1.343	0.229	1.170	0.394	1.180
5	1.68	0.345	2.850	0.324	1.704	0.176	1.704	0.188	1.536	0.315	1.575
6	2.83	0.253	3.770	0.339	2.111	0.132	2.111	0.133	2.027	0.228	2.010
7	4.75	0.206	4.240	0.330	2.407	0.100	2.407	0.100	2.321	0.167	2.315
8	8.00	0.162	4.678	0.331	2.509	0.089	2.509	0.088	2.429	0.133	2.485
9	13.45	0.129	5.010	0.313	2.509	0.089	2.509	0.083	2.473	0.127	2.515
10	22.63	0.132	4.980	0.312	2.500	0.090	2.500	0.083	2.473	0.134	2.480

APPENDICES

Sample No.	TIME (minutes)	Run 11D dic3 DTC 1/2*Dose	Collector Adsorption (mols E-6)	Run 12D dic3 DTC STD Cond	Collector Adsorption (mols E-6)	Run 13D no buffer STD Cond	Collector Adsorption (mols E-6)	Run 14D dic3 DTC STD Cond	Collector Adsorption (mols E-6)	Run 15D dic3 DTC 1/10 Dose	Collector Adsorption (mols E-6)
0	0.00	0.222	0.000	0.360	0.000	0.293	0.000	0.365	0.000	0.120	0.000
1	0.21	0.150	0.556	0.306	0.491	0.228	0.618	0.254	0.974	0.103	0.115
2	0.36	0.141	0.625	0.270	0.818	0.206	0.827	0.230	1.184	0.094	0.176
3	0.59	0.124	0.756	0.249	1.009	0.180	1.074	0.204	1.412	0.089	0.209
4	1.00	0.105	0.903	0.209	1.373	0.136	1.492	0.167	1.737	0.087	0.223
5	1.68	0.079	1.103	0.164	1.782	0.097	1.863	0.134	2.026	0.085	0.236
6	2.83	0.062	1.235	0.121	2.173	0.071	2.110	0.112	2.219	0.086	0.230
7	4.75	0.061	1.242	0.095	2.409	0.062	2.196	0.098	2.342	0.084	0.243
8	8.00	0.060	1.250	0.089	2.464	0.050	2.310	0.086	2.447	0.083	0.250
9	13.45	0.060	1.250	0.090	2.455	0.041	2.395	0.078	2.518	0.086	0.230
10	22.63	0.058	1.265	0.087	2.482	0.032	2.481	0.069	2.596	0.083	0.250

Sample No.	TIME (minutes)	Run 16D dic3 DTC 1/2 mineral	Collector Adsorption (mols E-6)	Run 17D dic3 DTC 1/2 mineral	Collector Adsorption (mols E-6)
0	0.00	0.345	0.000	0.345	0.000
1	0.21	0.312	0.611	0.312	0.611
2	0.36	0.303	0.778	0.303	0.778
3	0.59	0.290	1.019	0.293	0.963
4	1.00	0.277	1.259	0.279	1.222
5	1.68	0.255	1.667	0.262	1.537
6	2.83	0.230	2.130	0.231	2.111
7	4.75	0.191	2.852	0.186	2.944
8	8.00	0.142	3.759	0.138	3.833
9	13.45	0.112	4.315	0.107	4.407
10	22.63	0.085	4.815	0.088	4.759

These tables show the calculations for averaged results at standard conditions, for PNBX and for DiC3 DTC respectively.

Sample No.	TIME (minutes)	PNBX STD cond Run 2P	Run 3P	Average 2 & 3
0	0.00	0.392	0.392	0.392
1	0.21	0.367	0.343	0.355
2	0.36	0.317	0.326	0.322
3	0.59	0.294	0.301	0.298
4	1.00	0.257	0.276	0.267
5	1.68	0.206	0.225	0.216
6	2.83	0.134	0.170	0.152
7	4.75	0.061	0.087	0.074
8	8.00	0.021	0.019	0.020
9	13.45	0.010	0.009	0.010
10	22.63	0.010	0.008	0.009

Sample No.	TIME (minutes)	diC3 STD cond Run 1D	Run 9D	Run 12 D	Average 1, 9 & 12
0	0.00	0.360	0.360	0.360	0.360
1	0.21	0.295	0.299	0.306	0.300
2	0.36	0.266	0.283	0.270	0.273
3	0.59	0.252	0.263	0.249	0.255
4	1.00	0.222	0.229	0.209	0.220
5	1.68	0.173	0.188	0.164	0.175
6	2.83	0.132	0.133	0.121	0.129
7	4.75	0.097	0.100	0.095	0.097
8	8.00	0.092	0.088	0.089	0.090
9	13.45	0.081	0.083	0.090	0.085
10	22.63	0.082	0.083	0.087	0.084

Below are the calculations and values used in the comparison of the effects of eight times increase of energy, achieved through increased time and increased power. In each case, the averaged values for the standard conditions runs were used as the basis against which the others were calculated. Eight times the Time was achieved by taking standard conditions and reading the observation at eight times the Time.

PNBX Sample no.	Time (minutes)	Absorbency readings			Collector Adsorption			% improvement	
		Ave of STD	8 x Time	8 x Power	STD	8 x Time	8 x Power	8 x Time	8 x Power
0	0.00	0.39	0.39	0.39					
1	0.21	0.36	0.22	0.32	0.24	1.13	0.48	377.03	102.70
2	0.36	0.32	0.15	0.29	0.45	1.53	0.63	240.43	40.43
3	0.59	0.30	0.07	0.27	0.60	2.03	0.80	236.51	33.33
4	1.00	0.27	0.02	0.23	0.80	2.37	1.07	196.41	33.07
5	1.68	0.22	0.01	0.18	1.13	2.44	1.35	116.71	19.55
6	2.83	0.15	0.01	0.12	1.53	2.44	1.74	59.58	13.75
7	4.75	0.07	0.01	0.06	2.03	2.44	2.13	20.44	5.03
8	8.00	0.02	0.01	0.02	2.37	2.44	2.38	2.96	0.27
9	13.45	0.01	0.01	0.01	2.44	2.44	2.44	0.13	-0.13
10	22.63	0.01	0.01	0.01	2.44	2.44	2.42	0.00	-1.04



dic3 DTC Sample no.	Time (minutes)	Absorbency readings			Collector Adsorption			% improvement	
		Ave of STD	8 x Time	8 x Power	STD	8 x Time	8 x Power	8 x Time	8 x Power
0	0.00	0.36	0.36	0.36					
1	0.21	0.30	0.18	0.28	0.54	1.65	0.73	208.33	36.67
2	0.36	0.27	0.13	0.27	0.78	2.07	0.85	165.90	9.20
3	0.59	0.25	0.10	0.24	0.94	2.35	1.05	149.37	12.03
4	1.00	0.22	0.09	0.20	1.25	2.41	1.39	93.10	11.43
5	1.68	0.18	0.08	0.16	1.65	2.46	1.81	48.83	9.73
6	2.83	0.13	0.08	0.12	2.07	2.46	2.19	19.31	5.91
7	4.75	0.10	0.08	0.08	2.35	2.49	2.47	6.22	5.46
8	8.00	0.09	0.08	0.08	2.41	2.49	2.51	3.21	3.95
9	13.45	0.08	0.08	0.08	2.46	2.49	2.50	1.33	1.69
10	22.63	0.08	0.08	0.07	2.46	2.49	2.56	1.09	3.99